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# ANALYSIS OF MINERALS AND ORES OF THE RARER ELEMENTS

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# THE
# ANALYSIS OF MINERALS & ORES OF THE RARER ELEMENTS

## A MANUAL FOR ANALYTICAL CHEMISTS, METALLURGISTS, AND ADVANCED STUDENTS

BY

W. R. SCHOELLER
PH.D., F.I.C.

AND

A. R. POWELL

SECOND EDITION, ENTIRELY REWRITTEN

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# PREFACE.

It is the fate of this book to have been twice written in times of warlike stress. The first edition, which appeared 21 years ago, met with a favourable reception at a time when the analytical chemistry of the so-called rarer elements was beginning to acquire practical importance. Since then nearly all the elements in question have found important and permanent applications in the arts, while the analytical chemistry of the great majority has made such rapid strides that an adequate treatment of the subject has necessitated an almost complete rewriting of the original text.

A brief comparison between the two editions may interest the reader. No sooner had the first edition left the press than it became the object of a critical survey by us, with a view to attempting further progress in a field where so much remained to be done. Having reached the conclusion that none of the rarer elements presented more complex unsolved analytical problems than tantalum and niobium, we set out on a systematic investigation of earth-acid analysis. This task required 17 years' uninterrupted research work (1919–1936), the results of which were recorded in the *Analyst* in a series of 33 papers, and finally presented in the form of a monograph published under the auspices of the Society of Public Analysts. As an outcome of our work, we were able not only to discard all the older unsatisfactory procedures and literally write a new chapter in earth-acid analysis, but also to add fresh knowledge to the analytical chemistry of several mineral associates of tantalum and niobium, such as tungsten, titanium, zirconium, uranium, vanadium, and beryllium. These advances were achieved largely as the result of our application of tannin to the gravimetric analysis of these metals.

This manual is in the main the fruit of our practical experience, comparatively few processes being included with which we are not personally familiar. Thus, the section on the platinum metals (which also has been completely rewritten) may fairly claim to be the most up-to-date guide to the practical analysis of this group. Of the less familiar elements, the only two which have never come our way are rubidium and cæsium. We therefore enrolled the co-operation of Dr. Roger C. Wells, Chief Chemist of the U.S. Geological Survey—an authority on the rarer alkali metals—to revise the sections on lithium, rubidium, and cæsium.

The revision of the sections on molybdenum and tungsten was entrusted to Mr. D. A. Lambie, B.Sc., A.I.C., who has devoted much study and research to the analysis of these important metals. We are grateful to Mr. Lambie for his valuable help, which has lightened our labours.

The short section on radium which figured in the first edition has been omitted. We felt that the highly specialized subject of the radio-active elements—radium, mesothorium, protactinium, etc.—(like that of the noble gases of Group O) was out of place in a manual of inorganic analysis based upon classic chemical processes. It is interesting to note that the analytical chemistry of the two more plentiful radio-active elements thorium and uranium, whilst enriched to some extent with more accurate separation processes, has not undergone any profound change. Only in the case of lithium has no substantial addition or alteration been made; whilst two newcomers—hafnium and rhenium—have had to be accommodated in the present edition.

One radical change in the presentation of the text-matter has been found advisable. In the First Edition each element was considered separately; but, since certain elements are always found associated, we considered that it would be more helpful to the analyst if such elements were discussed in one and the same section. This has accordingly been done in the case of the following: rubidium and cæsium, the rare-earth metals, zirconium and hafnium, niobium and tantalum, selenium and tellurium, and the six platinum metals.

Another alteration has been made somewhat against our better judgment, the tabulated schemes for the complete analysis of minerals of the rarer elements now being replaced by succinct directions for carrying out this work. The reason is that, although we went to much trouble to compile these tables giving a maximum of information in a minimum of space, we have often heard the criticism that the tables were too difficult to follow. We may remind our critics of the recommendation made in our earlier Preface, that the operator himself should "map out the scheme after the model of the table" before undertaking the analysis. However, we have made the alteration in the hope that it will prove attractive to the majority of our readers.

The scope of the book has been enlarged by the inclusion of the analysis of ferro-alloys of vanadium, molybdenum, and tungsten, and the determination of these elements in steels, as well as the analysis of commercial selenium, tellurium, and platinum metals.

A separate Mineralogical Index has been retained, while the former "Index of Separations" has been replaced by a more elaborate "Analytical Index." Miss J. I. Lilley has given valuable assistance by preparing the greater part of the typescript.

W. R. S.,
A. R. P.

*August*, 1940.

# THE PERIODIC TABLE.

| Periods. | | Group 0. | Group I. | Group II. | Group III. | Group IV. | Group V. | Group VI. | Group VII. | Group VIII. |
|---|---|---|---|---|---|---|---|---|---|---|
| First short period | | **2 He**<br>4·003 | **1 H**<br>1·0080<br>**3 Li**<br>6·940 | **4 Be (Gl)**<br>9·02 | **5 B**<br>10·82 | **6 C**<br>12·010 | **7 N**<br>14·008 | **8 O**<br>16·0000 | **9 F**<br>19·00 | |
| Second short period | | **10 Ne**<br>20·183 | **11 Na**<br>22·997 | **12 Mg**<br>24·32 | **13 Al**<br>26·97 | **14 Si**<br>28·06 | **15 P**<br>30·98 | **16 S**<br>32·06 | **17 Cl**<br>35·457 | |
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| | Odd series | | **29 Cu**<br>63·57 | **30 Zn**<br>65·38 | **31 Ga**<br>69·72 | **32 Ge**<br>72·60 | **33 As**<br>74·91 | **34 Se**<br>78·96 | **35 Br**<br>79·916 | |
| Second long period | Even series | **36 Kr**<br>83·7 | **37 Rb**<br>85·48 | **38 Sr**<br>87·63 | **39 Y**<br>88·92 | **40 Zr**<br>91·22 | **41 Nb (Cb)**<br>92·91 | **42 Mo**<br>95·95 | **43 Ma**<br>... | **44 Ru 45 Rh 46 Pd**<br>101·7 102·91 106·7 |
| | Odd series | | **47 Ag**<br>107·880 | **48 Cd**<br>112·41 | **49 In**<br>114·76 | **50 Sn**<br>118·70 | **51 Sb**<br>121·76 | **52 Te**<br>127·61 | **53 I**<br>126·92 | |
| Third long period | Even series | **54 Xe**<br>131·3 | **55 Cs**<br>132·91 | **56 Ba**<br>137·36 | **57–71**<br>**Rare-earth Metals** | **72 Hf**<br>178·6 | **73 Ta**<br>180·88 | **74 W**<br>183·92 | **75 Re**<br>186·31 | **76 Os 77 Ir 78 Pt**<br>190·2 193·1 195·23 |
| | Odd series | | **79 Au**<br>197·2 | **80 Hg**<br>200·61 | **81 Tl**<br>204·39 | **82 Pb**<br>207·21 | **83 Bi**<br>209·00 | **84 Po**<br>[210] | **85**<br>... | |
| Fourth long period | Even series | **86 Rn**<br>222 | **87**<br>... | **88 Ra**<br>226·05 | **89 Ac**<br>... | **90 Th**<br>232·12 | **91 Pa**<br>231 | **92 U**<br>238·07 | | |

# CONTENTS.

SECTION PAGE

I.—INTRODUCTION . . . . . . 1
Note on References . . . . . . 1
(*a*) Crushing Samples for Analysis . . . 1
(*b*) Contamination in Crushing . . . . . 2
(*c*) Contamination by Fusion . . . . . 2
(*d*) The Jones Reductor . . . . . . 4
(*e*) Use of Filter-pulp in Analytical Work . . 4
(*f*) Application of Tannin in Gravimetric Analysis . 5
(*g*) Electromagnet . . . . . . 6

II.—MINERALOGICAL ANALYSIS . . . . . 7
(*a*) Water Concentration . . . . . . 8
(*b*) Separation by Heavy Liquids . . . 8
(*c*) Magnetic Separation . . . . . . 8
(*d*) Radioactivity . . . . . . 9
(*e*) Mineralogical Analysis of Alluvials . . . 9
(*f*) Examples of Mineralogical Analyses . . . 11
(*g*) Quantitative Mineralogical Analysis . . . 12
(*h*) Quantitative Mineralogical Analysis by Selective or Fractional Decomposition . . . . . 12

III.—QUALITATIVE CHEMICAL ANALYSIS . . 13

IV.—COMPLETE CHEMICAL ANALYSIS . . . 18
§ I. Methods for Determining Elements . . 18
§ II. Separation of Elements . . . . . 19
§ III. Other Methods of Separation . . . 27
§ IV. Separation into Insoluble Residue and Soluble Fraction . . . . . . 27
§ V. Determination of Heavy Metals . . . 30
§ VI. Separate Determination of Certain Constituents . 30
§ VII. Oxide Minerals . . . . . . 31
§ VIII. Mixed Oxide and Sulphide Ores . . 32
§ IX. Determinations by Difference . . . 35
§ X. Accuracy: " Traces " . . . . . 36

## SECTIONS V TO XXIII.

***These sections have been treated according to a uniform plan, each being divided into some or all of the following subsections (§§):***

**Minerals—Properties and Compounds—Quantitative Separation—Gravimetric Determination—Volumetric Determination—Colorimetric Determination—Detection in Minerals and Ores—Determination in Minerals and Ores—Determination of Impurities in Ores and Ferro-alloys—Complete Analysis of Minerals and Ores.**

*GROUP I.*

SECTION PAGE
V.—LITHIUM . . . . . . . 36
VI.—RUBIDIUM AND CÆSIUM . . . . . 41

*GROUP II.*

VII.—BERYLLIUM . . . . . . . 46

*GROUP III.*

VIII.—SCANDIUM . . . . . . . 57
IX.—GALLIUM . . . . . . . 60
X.—INDIUM . . . . . . . . 65
XI.—THALLIUM . . . . . . . 69
XII.—THE RARE-EARTH METALS . . . . . 74

*GROUP IV.*

XIII.—TITANIUM . . . . . . . 86
XIV.—ZIRCONIUM AND HAFNIUM . . . . 103
XV.—THORIUM . . . . . . . 117
XVI.—GERMANIUM . . . . . . . 123

*GROUP V.*

XVII.—VANADIUM . . . . . . . 129
XVIII.—NIOBIUM AND TANTALUM . . . . . 145

*GROUP VI.*

XIX.—SELENIUM AND TELLURIUM . . . . 166
XX.—MOLYBDENUM . . . . . . . 189
XXI.—TUNGSTEN . . . . . . . 207
XXII.—URANIUM . . . . . . . 220

*GROUP VII.*

XXIII.—RHENIUM . . . . . . . 238

*GROUP VIII.*

XXIV.—THE PLATINUM METALS . . . . . 240

*Owing to the complexity of the subject, the contents of this section are given in considerable detail below:*

SUBSECTION
§ I. Minerals . . . . . . . . 240
§ II. Properties and Compounds . . . . 242
§ III. Quantitative Separation . . . . . 247

A. ANALYTICAL TECHNIQUE.

SUBSECTION PARAGRAPH PAGE
(1) Importance of Dry Assaying in the Determination of the Platinum Metals . . . . . 249
(2) Treatment of the Lead Button . . . . 249
(3) Fusion with Lead in a Carbon Crucible . . 251
(4) Cupellation with Silver . . . . . 251
(5) Nitric-acid Parting of Silver Bead . . . 252
(6) Fusion of Silver Nitrate . . . . . 252
(7) Sulphuric-acid Parting of Silver Bead. . . 253
(8) Fusion with Silver in an Annealing Cup . . 253
(9) Solution in *Aqua Regia* . . . . . 253
(10) Precipitation with Ammonium Chloride . . 254
(11) The Chlorine Process . . . . . 255
(12) Ignition of Precipitates produced by Ammonium Chloride . . . . . . . . 255
(13) Reduction of Ignited Precipitates . . . 256
(14) Hydrogen-sulphide Precipitation . . . 256
(15) Zinc Precipitation . . . . . . 257
(16) The Nitrite Process . . . . . . 257
(17) Precipitation with Titanous Salt . . . 258
(18) Fusion with Sodium Peroxide . . . 258
(19) Fusion with Potassium Hydroxide and Nitrate . 259
(20) Distillation Apparatus for Osmium and Ruthenium . 259
(21) Recovery of the Non-volatile Platinum Metals from the Residual Solution . . . . . . 260
(22) Fusion with Sodium Chloride in a Current of Chlorine 260

B. SEPARATION OF THE PLATINUM METALS FROM OTHER ELEMENTS.

(23) From Silver . . . . . . . 261
(24) Rhodium from Silver . . . . . 261
(25) Palladium from Silver: Authors' Method . . 261
(26) Determination of Silver in the Presence of the Platinum Metals and Gold . . . . . . 262
(27) From Gold: by Parting . . . . . 262
(28) From Gold: Ferrous-chloride Reduction . . 262
(29) From Gold: Hydrazine Reduction . . . 263
(30) From Gold: Nitrite Reduction . . . 263
(31) From Gold: Ether Extraction . . . 263
(32) Determination of Gold in the Presence of the Platinum Metals . . . . . . . 263
(33) From Silver, Gold, Lead, Copper, Bismuth, etc. after Fusion with Lead . . . . . . 263
(34) Rhodium and Palladium from Lead . . . 265
(35) Rhodium, Palladium, Iridium, and Platinum from Lead 265
(36) From Copper: Thiocyanate Process . . . 266
(37) From Copper: Other Processes . . . 266
(38) From Bismuth . . . . . . 266
(39) From Arsenic, Antimony, Tellurium, and Selenium . 266
(40) From Iron, Nickel, Zinc, and Base Metals not precipitated by Zinc or Hydrogen Sulphide . . 267

SUBSECTION
PARAGRAPH PAGE

C. RESOLUTION OF THE PLATINUM GROUP INTO SUBGROUPS.

(41) Reactions of the Platinum Metals utilized in their Separation from One Another . . . 267
(42) Osmium from the Other Platinum Metals (and All Elements in general) . . . . . 269
(43) Osmium and Ruthenium from the Other Platinum Metals (and All Elements in general): Distillation in a Chlorine Current . . . . . 269
(44) Osmium-Ruthenium Distillation with Bromate . 271
(45) Iridium, Ruthenium, and Osmium from Platinum, Rhodium, and Palladium: Lead Fusion Method . 272
(46) Palladium from Platinum, Iridium, and Rhodium . 272
(47) Platinum from Iridium, Rhodium, and Palladium: Bromate Hydrolysis . . . . . 273
(48) Iridium from Rhodium, Palladium, and Platinum: Titanous Sulphate Method. . . . . 274
(49) Platinum and Iridium from Small Quantities of Palladium and Rhodium: Ammonium Chloride Method 275
(50) Rhodium from Platinum and Palladium . . 275

D. SEPARATION OF BINARY MIXTURES OF THE PLATINUM METALS.

(51) Osmium from Ruthenium . . . . . 276
(52) Platinum from Palladium . . . . . 276
(53) Platinum from Rhodium . . . . . 276
(54) Platinum from Iridium . . . . . 277
(55) Palladium from Rhodium . . . . . 278
(56) Palladium from Iridium . . . . . 278
(57) Rhodium from Iridium . . . . . 278

§ IV. **Gravimetric Determination** . . . . . 278

(58) Osmium: Precipitation as Hydroxide . . . . 278
(59) Osmium: Precipitation as Sulphide . . . . 279
(60) Ruthenium: Precipitation as Sulphide . . 279
(61) Ruthenium: Combination Process . . . . 280
(62) Platinum: Precipitation as Ammonium Chloroplatinate 280
(63) Platinum: Precipitation as Metal . . . 280
(64) Platinum: Precipitation as Sulphide . . . 280
(65) Iridium: Precipitation as Ammonium Chloriridate . 280
(66) Iridium: Precipitation as Hydroxide . . . . 281
(67) Iridium: Precipitation as Metal . . . . 281
(68) Palladium: Precipitation with Dimethylglyoxime . 281
(69) Palladium: Precipitation as Ammonium Chloropalladate 281
(70) Palladium: Precipitation as Sulphide . . . . 281
(71) Rhodium: Precipitation as Metal . . . . 282
(72) Rhodium: Precipitation as Hydroxide . . . 282
(73) Rhodium: Precipitation with Zinc or Magnesium . 282

§ V. **Volumetric and Colorimetric Determination** . . 282

(74) Platinum: Colorimetric Determination . . . 282
(75) Palladium: Colorimetric Determination . . . 283

SUBSECTION
PARAGRAPH PAGE
**§ VI. Detection in Ores** . . . . . . . 283
(76) Detection combined with Determination . . 283
(77) Association of the Platinum Metals in Nature . 283
(78) Detection in Base-metal Ores, Mattes, Slimes, Rocks, etc. . . . . . . . 283
(79) Detection in Alluvial Material . . . 284
(80) Specific Osmium Reactions . . . . 285
(81) Specific Ruthenium Reactions . . . 286
(82) Specific Rhodium Reactions . . . . 286
(83) Specific Iridium Reactions . . . . 287
(84) Specific Platinum Reactions . . . . 288
(85) Specific Palladium Reactions . . . . 288

**§ VII. Determination in Ores and Low-grade Raw Materials** . 288
(86) Determination in Base-metal Ores, Speisses, Sweeps, Rocks, etc. . . . . . . 288
(87) Silver Bead: Sulphuric-acid Parting . . . 289
(88) Silver Bead: Solution in Nitric Acid . . . 289
(89) Lead Button: Solution in Nitric Acid . . 290
(90) Determination in Copper-Nickel Ores, Mattes, and Copper Bullion . . . . . . 290

**§ VIII. Complete Analysis of Concentrates, Metals, and Alloys** 291
(91) Native Platinum . . . . . . 291
(92) South African Platinum Concentrates . . 293
(93) Osmiridium . . . . . . . 293
(94) Refined Platinum . . . . . . 294
(95) Palladium . . . . . . . 294
(96) Iridium . . . . . . . 294
(97) Rhodium . . . . . . . 295
(98) Osmium . . . . . . . 296
(99) Ruthenium . . . . . . . 296
(100) Contact Points and Platinum Crucibles . . 296
(101) Dental Alloys . . . . . . 296
(102) Jewellers' Platinum Alloys . . . . 296

INTERNATIONAL ATOMIC WEIGHTS, 1940 . . . . 297

GRAVIMETRIC FACTORS . . . . . . . 298

MINERALOGICAL INDEX . . . . . . . 300

ANALYTICAL INDEX . . . . . . . . 302

# THE
# ANALYSIS OF MINERALS AND ORES OF THE RARER ELEMENTS.

## I.—INTRODUCTION.

GENERAL information concerning certain manipulations and apparatus, of importance in mineral analysis, has been placed in this introductory section.

**Note on References.**—References to original papers and books are given in the customary manner in footnotes, but for the sake of brevity the following three books will be referred to as follows:

(1) *Applied Inorganic Analysis*, by W. F. Hillebrand and G. E. F. Lundell; New York, 1929: as " Hillebrand and Lundell, *op. cit.*"

(2) *The Analytical Chemistry of Tantalum and Niobium*, by W. R. Schoeller; London, 1937: as " Schoeller, *op. cit.*"

(3) *Ausgewählte Methoden für Schiedsanalysen und kontradiktorisches Arbeiten*, by the Committee of the *Gesellschaft deutscher Metallhütten- und Bergleute e. V.*, Second Edition; Berlin, 1931: as " *Ausgew. Methoden.*"

**(a) Crushing Samples for Analysis.**—The success of a mineral analysis depends in many cases on the amount of care with which the crushing has been carried out. If the material is a sulphide ore, fine grinding is not so essential, a fineness of −100-mesh being in most cases sufficient. Oxide minerals, however, require much more elaborate grinding, especially the crystallized varieties found in metamorphic rocks and alluvials. Such material must be crushed to an impalpable powder, which is best done in the following manner: The sample is first crushed to −100-mesh size as usual, screened, and carefully quartered down until the weight is reduced to 2–3 g. This is placed in an agate mortar, and enough water added to form a thick paste, which is thoroughly ground for fifteen minutes or until all grittiness has disappeared. The contents of the mortar are then transferred to a flat basin with a minimum of distilled water from a wash-bottle; the dish is given a rotary motion, and the water slowly decanted into a similar basin. Washing and decantation are repeated until the slimed material has been separated from the fine sandy matter. The latter is rinsed back into the mortar with very little water, again ground, and all the operations repeated until the whole of the sample has been slimed. The aqueous suspension is evaporated to dryness on a steam-bath; the residue after thorough mixing is ready for weighing.

In many cases, especially with minerals containing ferrous compounds, it is advisable to grind the sample under absolute alcohol free from fixed residue, and to allow the alcohol to evaporate at room temperature. These precautions have been found necessary to prevent oxidation of the fine powder during crushing and drying.

(**b**) **Contamination in Crushing.**—When a mineral is being crushed or ground it tends to exert an abrading action on the grinding surfaces, and if it is harder than the material of the crusher, a more or less considerable amount of the latter will find its way into the sample. Contamination is greater in the case of friction than when concussion is employed. Thus a muller and slab (bucking plate) should not be used for any but very soft materials; it has its use in preparing samples for works assays, but the risk of contamination is too great for exact analytical work. A cast-iron or steel mortar answers well for breaking up lumps by pounding, but it should be carefully tested for its resistance to abrasion by friction, by means of quartz powder or sand previously extracted with strong hydrochloric acid. Porcelain or Wedgwood mortars and pestles suffer a decided loss when used on material the hardness of which exceeds 6. Agate is most commonly used for fine grinding, but it is likewise worn away by minerals of hardness 7 and over. For such products, the best procedure consists in grinding them in a steel mortar that has been in use for some time, and extracting the fine powder under water with a horseshoe magnet or magnetized knife-blade. This mode of working is not applicable to ores containing strongly magnetic minerals, *e.g.* magnetite. The hardest minerals being almost invariably insoluble in acids, the powder may also be extracted with very weak hydrochloric acid or, what is preferable, iodine water. The procedure to be adopted depends on the nature of the material.

(**c**) **Contamination by Fusion.**—This may be due to (1) corrosion of the crucible, or (2) impurities in the fluxes used.

(1) *Corrosion of the Crucible.*—*Platinum* is slightly attacked by fused alkali carbonate, more so by bisulphate or nitrate, and rather strongly by cyanide, hydroxide, or peroxide. The metal introduced into the analysis is eliminated by precipitation with hydrogen sulphide.

*Silver* crucibles are very useful for fusions with alkali hydroxide and nitrate; though a little silver goes into solution, it is readily eliminated as chloride or sulphide. The metal being easily obtained in the pure state, no other impurities are introduced through the use of a crucible obtained from a reliable source. The decomposition of silicates can be accomplished by fusion with sodium hydroxide in a silver crucible; the only precaution to be observed is, not to use a blast, Teclu, or other powerful burner, for fear of melting the silver.

*Copper* is a very good substitute for silver; the metal is almost chemically pure, and though a good deal of attack takes place in a peroxide fusion, the removal of the dissolved copper by hydrogen sulphide gives no trouble.

*Nickel* crucibles are widely used for peroxide fusions in the determination of single constituents. They must not be employed for fusion assays involving the estimation of base metals, because the degree of purity of the metal is rather uncertain. Thus a crucible analysed by one of the authors (" Reinnickel " brand) was found to contain 0·14 per cent. of copper, 0·31 of iron, 0·31 of manganese, 0·07 of cobalt, and 0·06 of magnesium. Silicon also is a likely impurity. The above remarks apply also to *iron* crucibles.

According to Brunck and Höltje,[1] nickel crucibles can be used as a substitute for platinum crucibles for the decomposition of a great variety of minerals by fusion with alkali ; the flux used is sodium hydroxide in the form of pellets. The fusion is carried out below 500° C., a temperature at which the nickel is hardly attacked. The alkali (5 g.) is dehydrated by fusion, and allowed to solidify; the finely powdered, weighed mineral is added, and decomposed at a sintering temperature; the heat is slowly raised, and kept for 10 to 15 minutes below a visible red. The crucible should be supported by a perforated asbestos board, with the bottom protruding a few millimetres below the opening. The cold melt is disintegrated with hot water, the contents of the crucible are rinsed into a basin, and any material adhering to the crucible is removed after drying by a second fusion with 0·5 g. of alkali.

Brunck and Höltje state that all silicates are thus decomposed in 10 to 20 minutes. Bauxite is easily attacked, and need not be finely crushed. Chromite requires addition of sodium nitrate; cassiterite a little cyanide. The attack on corundum and spinels is poor.

*Silica* crucibles cannot, of course, be used for fusions with alkaline fluxes, but are most serviceable for bisulphate fusions. It appears from statements in the literature that porcelain crucibles also are used for such fusions, but there can be no doubt that " Vitreosil " crucibles, in spite of their higher cost, are much cheaper in the long run, as one and the same crucible can be used for some hundreds of fusions, with very little loss in weight. The amount of silica taken up by the flux is of the order of 0·0002 g. per fusion[2]; in other words, it is negligible for practical purposes. A platinum crucible, on the other hand, loses about 0·002 g. in a bisulphate fusion, and the metal thus introduced into the solution contaminates sulphide and ammonia precipitates, which usually require purification. Another disadvantage of platinum crucibles is the foaming of the pyrosulphate, necessitating gradual and hence more protracted heating. According to the usual text-book statements, a bisulphate fusion occupies 2 to 4 hours or more, but we carry out the operation in 5 to 10 minutes by using a silica crucible and heating it on an asbestos mat until the flux is fused. The crucible is then held over a free flame and gently swirled while the heat is gradually raised. Treated in this manner, ignited oxide precipitates dissolve in a few minutes provided they are in a state of fine subdivision, which is ensured by the incorporation of filter-fibre before or after precipitation (**e**, *below*). The most refractory oxide, in our experience, is ignited beryllia, which requires 10 minutes' fusion with excess of potassium pyrosulphate over a strong Bunsen burner.

We give preference to the potassium salt, because sodium pyrosulphate loses sulphur trioxide and solidifies at a lower temperature. The sodium salt should, however, be used for fusions involving the rare earths, and for the decomposition of chromite, which it readily attacks[1] while obviating the formation of the more or less insoluble potassium chromium sulphate.

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[1] O. Brunck and R. Höltje, *Angew. Chem.*, 1932, **45**, 331; *Zeitsch. anal. Chem.*, 1933, **94**, 340.

[2] H. S. Washington (*The Chemical Analysis of Rocks* (4th edition. New York, 1930), p. 178) gives the loss as 0·02 to 0·04 g. for an ordinary fusion, but this is an uncorrected misprint which Dr. Washington requested the senior author to rectify in his review of the work (*Analyst*, 1931, **56**, 278); the correct figure is 0·0002 to 0·0004 g.

(2) *Impurities in the Fluxes.*—Contamination due to this cause can be guarded against and allowed for by blank tests on every fresh supply of material, even that sold as chemically pure. If the blank result is excessive, the bottle should be rejected. Until quite recently it was difficult to obtain chemically pure potassium (sodium) cyanide, but reagents of A.R. grade are now on the market. The ordinary article is contaminated with sulphide, which can be detected and removed from the solution by agitation with a little bismuth hydroxide, followed by filtration. The darkening of the white precipitate indicates the presence of sulphide.

**(d) The Jones Reductor.**[2]—This apparatus is very convenient for the rapid reduction of solutions of metallic compounds. It consists of a cylindrical funnel (100 ml. capacity) mounted on a glass tube 18 in. long and 0·5 in. wide; the lower, drawn-out end carries a glass tap, below which it reaches through a rubber stopper almost to the bottom of a vacuum filtration flask. The lower end of the 0·5-in. tube above the tap contains a perforated porcelain plate supporting a pad of glass-wool or a 1-in. layer of coarsely powdered calcined quartz, on which rests a column of pure 20- to 30-mesh amalgamated zinc.

The reductor is prepared for use by being filled with 100 ml. of cold 5 per cent. sulphuric acid, and the tap is opened slightly while suction is applied, a slow current of acid flowing through the zinc. The latter is then washed 5 times with water, and the tap closed while the tube is full of water. The filtration flask is then emptied and washed. The acid wash is always applied before use.

To carry out a reduction, the solution is transferred to the funnel and slowly drawn through the zinc column. When the funnel is nearly empty its sides are rinsed down, after which the reductor is washed with dilute acid followed by water as *above*, care being taken to keep the zinc column always covered with liquid. When the solution has been titrated the reductor is again ready for use. The deduction for iron in the zinc, if any, must be ascertained by a blank test.

**(e) Use of Filter-pulp in Analytical Work.**—The use of filter-pulp for facilitating the filtration of flocculent or gelatinous precipitates such as ferric and aluminium hydroxides was first proposed by M. Dittrich.[3] The advantages resulting from the employment of filter-pulp are so striking and manifold that its application has now been extended to the filtration of all the more intractable suspensions, as of gelatinous silica, finely divided barium sulphate, sulphides, sulphur, slimy ferrocyanides, ammonium uranate, colloidal hydrated oxides, etc. The incorporation of filter-pulp with a precipitate further ensures its retention on the filter and facilitates the cleaning of the beaker on account of its scouring action; ignition of the precipitate gives a finely divided powder which rapidly acquires constant weight and is readily attacked by fluxes in a subsequent fusion.

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[1] W. Erber, *Angew. Chem.*, 1937, **50**, 382.

[2] C. Jones, *Trans. Amer. Inst. Mining Eng.*, 1888, **17**, 411.

[3] *Ber.*, 1904, **37**, 1840.

Filter-pulp, or macerated filter-fibre, is prepared by trituration of the clippings of high-grade ashless Whatman filter-paper (which are sold specially for the purpose) with distilled water in a porcelain mortar. It is kept ready for use in a wide-mouthed bottle in two forms, *viz.* a thick pulp, used as a filtering medium, and a thin cream, which is stirred into solutions either before or after precipitation and is applied to the beaker when this is cleaned with a rubber-tipped glass rod.

A pad of filter-pulp gently pressed into the apex of a paper filter acts as an efficient filter-bed, replacing the unsatisfactory double filter; the familiar cloudiness of filtrate so often observed when the insoluble portion of a finely ground ore is filtered off and washed after an acid attack is easily prevented by the use of this expedient. If a precipitate is not required for gravimetric work, the filter-paper may be dispensed with, the pad being pressed loosely or tightly into the funnel according to the desired speed of filtration and the nature of the precipitate under treatment. Gelatinous silica is readily filtered off when mixed with creamed filter-fibre and collected on a fairly thick, loose pulp bed.

The creamed filter-pulp which it is intended to incorporate with a precipitate may also be poured into the filter on which the precipitate will be collected, the suspension being stirred up with the glass rod at each fresh addition. This is a useful time-saving procedure in the case of precipitates produced without addition of filter-pulp, as they need not be disturbed after having settled in the beaker.

It should be borne in mind that strong acids act upon cellulose with formation of soluble hydroxy-compounds, which prevent the precipitation of metals by ammonia.[1] The formation of such compounds takes place when solutions containing filter-pulp and sulphuric as well as nitric acid are evaporated. If the evaporation is prolonged on the water-bath until the nitric acid is expelled, the presence of as little as 0·1 ml. of sulphuric acid causes slightly low results. The soluble ferric complex is completely precipitated by ammonium sulphide, while the aluminium complex must be destroyed by strong heating with nitric and sulphuric acids. Presumably these complexes are amenable to tannin precipitation, as are those of all the organic hydroxy-acids so far investigated (f, *below*).

**(f) Application of Tannin in Gravimetric Analysis.**[2]—Under the name of "tincture of galls," tannin was employed as a qualitative reagent more than a hundred years ago, but it gradually fell into disuse, and by the beginning of the present century was applied in metallurgical work merely as an indicator in Alexander's molybdate method for the determination of lead. Our method for the separation of tantalum from niobium, published in 1925,[3] inaugurated a series of investigations which proved tannin to be a quantitative reagent of cardinal importance for the separation and determination of a number of rarer and more common elements, principally those of the ammonia group not precipitated by ammonia or ammonium sulphide from tartrate solution. The aqueous solution of tannin, being a colloidal suspension of negatively charged particles, precipitates positively charged metallic hydroxide particles; the resultant adsorption complexes flocculate remarkably well and are quite insoluble. Though voluminous, they are readily filtered off and washed (especially when mixed with filter-pulp), and upon ignition are converted into weighable oxides. The tannin complexes of some elements are colourless, but others are brilliantly and characteristically coloured, a factor of the greatest quantitative and qualitative importance. The most remarkable peculiarity of the reactions under discussion is, that the precipitation is not inhibited by the presence of an organic hydroxy-acid (tartaric, citric, etc.). Whilst the theory of the action of tannin upon solutions of the metallic tartaro- (and other) complexes is still obscure, its practical application is of great value in the analytical chemistry of such " rarer " elements as tantalum, niobium, titanium, zirconium, thorium, vanadium, uranium, etc. The processes utilizing tannin are described under the headings of these and other elements.

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[1] E. Wilke-Dörfurt and E. Locher, *Zeitsch. anal. Chem.*, 1924, **64**, 436.
[2] Schoeller, *op. cit.*, pp. 145–169.
[3] *Analyst*, 1925, **50**, 485.

The most interesting tannin reactions are those occurring in oxalate solution, in which precipitation of the tannin complexes takes place at more or less marked acidity intervals. This differential behaviour has enabled us to distinguish between two groups of elements, Group A being quantitatively separable from Group B by suitable adjustment of the acidity (see **XIII,** preamble to § III). The separation of tantalum from niobium (both members of Group A) by tannin (*q.v.*) is based upon the same principle.

The following classification of the tannin complexes into three groups, based upon the solubility of the precipitates in acids, is of practical interest:

*Group A* (tantalum: yellow; titanium: red; niobium: red; tungsten: brown).—The complexes of tantalum, niobium, and tungsten are insoluble, the titanium complex is soluble, in dilute sulphuric acid. The complexes of tantalum, titanium, and niobium are insoluble in feebly acid oxalate solution half saturated with ammonium chloride. The tungsten complex is the only one not precipitated alone from solutions containing organic acids, but partial precipitation is induced by the other elements of Group A.

*Group B* (vanadium: bluish-black; iron: purplish-black; zirconium, thorium, and aluminium: colourless; chromium: greenish; uranium: brown).—Soluble in feebly acid oxalate solution half saturated with ammonium chloride; insoluble in ammoniacal oxalate solution. Insoluble in feebly acid tartrate solution.

*Group C* (rare-earth metals: colourless, the cerium complex darkening on exposure; beryllium: colourless; manganese: darkens on exposure, like cerium).—Soluble in feebly acid tartrate solution; insoluble in ammoniacal tartrate solution.

(g) **Electromagnet.**—This instrument is indispensable in mineralogical analysis (**II,** *below*). The particulars given *below* refer to a magnet described by R. H. Richards,[1] but modified so as to attract the more weakly magnetic minerals.

The magnet itself consists of two cores of slowly annealed iron, joined at the top by a yoke of cast-iron. The pole shoes are slotted, to allow of adjustment of the air gap, and bevelled towards each other at an angle of

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[1] *Text Book of Ore Dressing*, 1909, p. 609.

45°. Each core is wound with 5000 ft. of No. 21 cotton-covered copper wire, making 6760 coils. The turns are held in place top and bottom by brass rings, and are protected by layers of paper and tarred marline. The magnet is run on a 110-volt circuit, and by the introduction of suitable resistances in series its strength may be so adjusted as to effect separation of a mineral mixture into fractions of different magnetic susceptibility.

The separation of the more important magnetic minerals by means of the above electromagnet may be effected by inserting the following resistances:

(*a*) 16 candle-power lamp, 50 volts; resistance about 96 ohms.
(*b*) 16 „ „ „ 50 „ „ „ 96 „
(*c*) 8 „ „ „ 50 „ „ „ 48 „
(*d*) 8 „ „ „ 50 „ „ „ 48 „

The mode of applying the resistances, and the selective attraction exerted on various minerals, are as follows:

| Resistances in Circuit. | Approximate Current (amp.). | Mineral Attracted. |
|---|---|---|
| *a*+*b*+*c*+*d* . . | 0·27 | Ilmenite |
| *a*+*b*+*c* . . . | 0·37 | Garnet |
| *a*+*b* . . . | 0·55 | Wolfram |
| *a* . . . . . | 0·75 | Monazite |
| All out . . . | 1·1 | Stannine |

## II.—MINERALOGICAL ANALYSIS.

A THOROUGH knowledge of mineralogy is indispensable to the metallurgical chemist for solving the problems relating to the economic recovery of the valuable constituents of ores. To take a well-known example: If an ore be found to contain substantial amounts of tin and tungstic acid, it becomes more important to identify the form in which the latter occurs than to ascertain its percentage in the ore; for a tin-wolfram ore is valuable for both its tin and tungsten contents, whereas certain grades of tin-scheelite ore are, up to the present, almost worthless.

In the laboratory, the application of the determinative methods of mineralogy constitutes a most valuable help in analytical work. A qualitative analysis is not only supplemented, but may be entirely replaced, by a mineralogical examination. The latter is both quicker and simpler, because it substitutes mechanical separation and simple tests (physical, blowpipe, etc.) on the picked fragments of mineral, for the elaborate operations of opening up, separating into groups, resolving these into elements, and identifying the latter. It is also more delicate, because a few particles or crystals of a mineral occurring in traces can be picked out and identified in a sample weighing many pounds; in chemical analysis this small quantity would probably be overlooked. Finally, it conveys information as to the mode of combination of elements in an ore mixture which chemical analysis cannot give, since the latter starts by destroying the mineral constituents.

It has been mentioned that mineralogical separation is done by mechanical means. Even separation may often be dispensed with, *e.g.* when the ore under investigation is in the form of coarse lumps, and the operator possesses sufficient experience to recognize mineral species by inspection, aided, if necessary, by determination of the hardness, streak, cleavage, etc. The coarse lumps are next broken up to expose fresh surfaces: in this manner all the minerals present can be identified in lump ore. Since fine grinding obliterates the megascopic characteristics of a mineral mixture, crushing previous to analysis should only be done after the nature of an ore has been satisfactorily ascertained. When asked to report on an ore, the chemist should insist on receiving it in a natural or coarse condition.

The more important rarer elements are extracted from detrital deposits formed by the disintegration of igneous and metamorphic rocks in which these elements occur in minute quantities.[1] The minerals containing them, being heavier and more resistant to atmospheric agencies than the mother rock, have been accumulated in river beds and on sea and lake shores during the present and past geological periods, the deposits being known as alluvials, placers, black sands, etc. They occur in every degree of comminution, generally in the form of water-worn, rounded or flattened grains. On account of their importance as a source of many rarer elements, a mineralogical analysis of alluvial deposits is frequently necessary. The separation of the material into its component minerals is based upon differences in their physical properties.

The more important operations in mineralogical analysis are:

(a) **Water Concentration.**—In the case of alluvials, this has been effected by Nature. In the laboratory, it is carried out by panning, on a larger scale by jigs and shaking-tables.

(b) **Separation by heavy liquids,** such as bromoform (sp. gr. 2·9), methylene iodide (3·33), mercury potassium iodide solution (3·17), cadmium borotungstate solution (3·28). The mineral mixture is sprinkled upon the liquid contained in an ordinary funnel, the lower end of which carries a rubber tube closed by means of a pinchcock.

(c) **Magnetic Separation.**—The following minerals are attracted by a horseshoe magnet: magnetite, certain varieties of hæmatite, and a few mixed oxides such as titaniferous magnetite, jacobsite, $(Mn, Mg)O \cdot (Fe, Mn)_2O_3$, manganoferrite, $(Mn, Fe)O \cdot (Fe, Mn)_2O_3$, and magnoferrite, $MgO \cdot Fe_2O_3$; pyrrhotite; and ferriferous platinum.

The minerals attracted by an electromagnet are more numerous. They may be subdivided into strongly, moderately, and weakly magnetic, according to their susceptibility at various current densities (**I, g**). The subdivision is only approximate, as the magnetic susceptibility of a mineral species varies with its chemical composition. Thus, the following minerals not normally found in alluvials are generally, but not invariably, attracted by an electromagnet: chalybite, hæmatite, limonite, franklinite, biotite, hornblende, augite, epidote, olivine, and serpentine. Generally speaking, the magnetism of a mineral is due to its iron or ferrous-oxide content (monazite owes its susceptibility to cerium). Native platinum, even if not attracted by a horseshoe magnet (*above*), reacts to an electromagnet, usually leaving a very small non-magnetic reject. Minerals of the columbite-tantalite series (*q.v.*) are more or less susceptible, according to the relative proportions of ferrous and manganous oxides in the molecule $(Fe, Mn)O \cdot (Nb, Ta)_2O_5$, ferrocolumbite (-tantalite) being more magnetic than manganocolumbite (-tantalite). The common varieties of garnet, being ferruginous, are attracted by an electromagnet; pure rutile, cassiterite, and zinc blende do not react, but the ferriferous varieties are attracted.

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[1] The rarer elements not found in metamorphic rocks occur in very minute quantities in sulphide ores such as zinc blende, copper and nickel ores, pyrites, pyrrhotite, etc. They are gallium, germanium, indium, and thallium; selenium and tellurium. Traces of platinum metals are also found in pyrrhotite, etc., as well as in igneous rocks.

Titanium, zirconium, and vanadium are universally found in small quantities in rocks of various description.

Lithium, cæsium, and rubidium are primarily found in micas and felspars, and are dissolved in the weathering of the mother rock.

(d) **Radioactivity** [1] is tested for, if no electroscope is available, by means of a photographic plate. The fractions obtained in the analysis are disposed along lines in the shape of numerals on the black paper wrapping containing the plate; this is left in the dark for 12 to 48 hours, after which the negative is developed and fixed in the ordinary way, when the design will be reproduced in dark lines if radioactive minerals are present.

(e) **Mineralogical Analysis of Alluvials.**—The scheme given *below* is based on differences in magnetic properties, colour, and specific gravity.

If the material contains coarse particles, it is first passed through a sieve (8-, 10-, or 12-mesh) and the oversize sorted by hand into homogeneous fractions. The undersize is submitted to electromagnetic separation. The non-magnetic fraction is separated by means of bromoform if quartz apparently predominates; if not, it is first sorted with the help of forceps into coloured and colourless fractions, and the latter separated by bromoform. The magnetic fraction is further divided into strongly and weakly magnetic portions; each of these is then sorted. When apparently homogeneous fractions have been obtained, they are identified by mineralogical or, if necessary, chemical tests. Small particles are tested for their streak by being crushed with a knife-blade on the streak-plate. If the sand is very fine, the fractions are examined under a low-power microscope (1½ in.) in reflected as well as in transmitted light.

## TABLE FOR THE EXAMINATION OF ALLUVIALS.[2]

### A. NON-MAGNETIC MINERALS.

(1) **Of Metallic Appearance :**

*Gold*: characteristic colour; sectile.
*Osmiridium* (*q.v.*).
*Molybdenite* (*q.v.*).
*Platinum*: usually magnetic (B (1), *below*).

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[1] For radioactive minerals, see **XV, XVIII,** and **XXII.**

[2] For the description of minerals of the rarer elements, consult the text under "Minerals"; for qualitative tests, see "Detection in Minerals."

(2) **Dark, Opaque :**

*Cassiterite*: streak colourless, or nearly so. Treated with zinc dust and hydrochloric acid, the particles acquire a tin-white coating which can be polished.
*Rutile* (*q.v.*): pale brown streak.

(3) **Coloured :**

Paler varieties of cassiterite and rutile: see (2).
*Titanite* or *sphene* (*q.v.*): brownish, streak white.
*Chrysoberyl* (*q.v.*): greenish, streak white.
*Corundum*: hardness 9, various colours.
*Beryl*: see (4).
*Baddeleyite* (*q.v.*): grey or brown: zirconium reaction with ammonium phosphate.
*Zircon* (*q.v.*): red, brown, smoky. Characteristic appearance under microscope: square prism with pyramidal terminations.

(4) **Colourless, or Slightly Coloured :**

(α) *Lighter than bromoform*:
  *Quartz and its varieties.*
  *Beryl* (*q.v.*): green to white.
(β) *Heavier than bromoform*:
  *Scheelite* (*q.v.*): boiled with hydrochloric acid, the particles assume a canary-yellow colour.
  *Zircon* (*q.v.*): pale pink (see also (3)); appearance under microscope (*cf.* (3), *above*).
  *Topaz*: wine-yellow, hardness 8; gives fluorine reaction.
  *Apatite*: greenish to white. Reactions for fluorine, chlorine, phosphoric acid.
  *Diamond*: transparent, highly refractive. Hardness 10.

## B. MAGNETIC MINERALS.

(1) **Strongly to Moderately Magnetic :**

(α) *Brown to black, opaque*:
  *Magnetite*: black, attracted by knife-blade.
  *Ilmenite* (*q.v.*): black; streak black to brownish; titanium reactions.
  *Menaccanite, iserine*: varieties of ilmenite.
  *Chromite*: brown streak. Green borax bead.
  *Wolframite* (*q.v.*): brown streak. The powder turns yellow when boiled with *aqua regia*.
  *Columbite, tantalite* (*q.v.*): brown streak. Reactions for earth acids (**XVIII**).
  *Black garnet*: fusible.
(β) *Coloured*:
  *Garnet*: generally red to pink, also brownish. Rhombic dodecahedra frequent.

(γ) *Of Metallic Appearance*:
*Platinum* (*q.v.*).

(2) **Weakly Magnetic :**

(α) *Black, Opaque*:
*Pleonaste*: black spinel; colourless streak; infusible.
*Schorl*: black tourmaline; colourless streak; reaction for boric acid.
*Emery*: greyish-black corundum.

(β) *Coloured*:
*Spinel*: generally red, resembling garnet, but infusible.
*Tourmaline*: blue, green, red ((α), *above*).
*Monazite*: pale yellow, golden-yellow to dark reddish-brown; radioactive. Reactions for phosphoric acid and rare earths.

**(f) Examples of Mineralogical Analyses.**—Two examples of mineralogical analyses from actual practice are given *below*, since it is difficult to outline a systematic procedure applicable in all cases.

*Example A.*—All finer than 12-mesh. Electromagnetic separation gave:

| | | | | |
|---|---|---|---|---|
| (*a*) Non-magnetic fraction | 69·3 | per cent., | sp. gr. | 6·7. |
| (*b*) Weakly magnetic „ | 21·3 | „ | „ | 5·4. |
| (*c*) Strongly „ „ | 9·4 | „ | „ | 5·0. |

(*a*) The non-magnetic fraction was treated with zinc dust and acid, and the few colourless particles picked out from among those of metallic appearance (*i.e. cassiterite*); they were separated by bromoform into *quartz* and *topaz* (fluorine reaction).

(*b*) The weakly magnetic fraction was sorted into two homogeneous portions: (α) the bulk consisted of dull black water-worn grains. After powdering and fusing with bisulphate, strong niobium reactions were obtained, tantalum being subordinate. These and the low specific gravity prove *columbite*. (β) Subordinate fraction: brown, opaque, soft, water-worn grains, giving titanium reactions: *iserine*.

(*c*) The strongly magnetic fraction was hand-sorted into five homogeneous portions: (α) pale pink transparent grains, and (β) red transparent grains. Both these were found to consist of *garnet* rich in manganese (*spessartite*). (γ) Dull black grains, identical with *columbite* of fraction (*b*). (δ) Brown grains identical with *iserine* of fraction (*b*). (ε) Black, lustrous, angular particles found to consist of *ilmenite*.

*Example B.*—The sample was screened through a 10-mesh sieve. The oversize, part of which gave a brown, and part a colourless, streak, was treated with zinc dust and acid as in the previous case. The non-metallic-looking black particles were found to give strong tantalum, but no niobium reactions; sp. gr. 7·1; hence *tantalite*. The metallic-looking particles constituting the bulk were *cassiterite*. The undersize was treated electromagnetically. The strongly and weakly magnetic products looked very similar, and were united previous to hand-sorting. They contained chiefly *ilmenite* and a little *garnet*; some more *tantalite* was also found. The non-magnetic portion was sorted according to appearance into: (α) black grains, found to be *cassiterite*; (β) a subordinate amount of *muscovite*; (γ) a few tiny grains of *gold*; and (δ) colourless particles. These were treated with bromoform, giving *quartz* as the lighter mineral, and a small heavy fraction which became yellow on boiling with hydrochloric acid: *scheelite*.

**(g) Quantitative Mineralogical Analysis.**—A quantitative mineralogical analysis of alluvial material is often required. The procedure is the same as that outlined *above*; in addition, every product is weighed. The identification tests are carried out after the products have been separated and weighed.

*Example C.*—A little over 2 g. of sand was available. It was separated electromagnetically into:

| | | |
|---|---|---|
| (*a*) | Strongly magnetic fraction, | 0·23 g. |
| (*b*) | Weakly ,, ,, | 0·04 g. |
| (*c*) | Non-magnetic ,, | 2·04 g. |
| | Total . . | 2·31 g. |

(*a*) This product was homogeneous and brownish-black; no magnetite was found (knife-blade test). It was identified as *ilmenite*.

(*b*) This was of a pale brown colour. After fusing with bisulphate, one-half of the solution was tested with molybdate solution, the other half with ammonium oxalate: positive tests for phosphoric acid and rare earths proved *monazite*.

(*c*) The non-magnetic portion (practically colourless: absence of cassiterite) was separated by bromoform, the lighter portion (*quartz*) weighing 1·92 g. The heavy product (pale pink) was fused with sodium peroxide, the acidified solution giving strong zirconium reaction: *zircon*. Hence the composition of this alluvial was:

| | |
|---|---|
| Ilmenite . . . . . . . | 10·0 per cent. |
| Monazite . . . . . . . | 1·7 ,, ,, |
| Zircon . . . . . . . | 5·2 ,, ,, |
| Quartz . . . . . . . | 83·1 ,, ,, |
| | 100·0 per cent. |

**(h) Quantitative Mineralogical Analysis by Selective or Fractional Decomposition.**—This procedure, the principle of which is explained under IV, § VIII, 4, is of limited applicability in the case of minerals of the rarer elements, because the majority have to be opened up by fusion. The weighed quantity of material is treated with the solvent and filtered on a porous crucible; the insoluble residue is washed off, dried, and weighed, and the dissolved mineral taken by difference. The following are examples of this class of work: Separation of tungstic ochre from wolfram and scheelite by hot dilute caustic soda, tungstic ochre dissolving. Separation of wolfram from scheelite (finely powdered) by nitric acid, followed by filtration and treatment with ammonia: wolfram is left almost unattacked; the separation is not quite quantitative. Separation of molybdite from molybdenite by hydrochloric acid, in which the latter is insoluble. Separation of bismuth from molybdenite by weak nitric acid, which dissolves bismuth. Separation of molybdenite from galena by hot hydrochloric acid (1 : 1), which dissolves the latter.

Further examples of chemical separations of minerals of the commoner elements will be found in Table XI, p. 34. Generally speaking, dilute hydrochloric or organic acids are used as solvents for carbonates; nitric acid for sulphides; and hydrofluoric acid for silicates.

## III.—QUALITATIVE CHEMICAL ANALYSIS.

TESTS and characteristic reactions for the detection of each of the rarer elements discussed in this book will be described in every individual case. It is intended here to present a general scheme of systematic qualitative analysis applicable to any ore or mineral mixture, and including nearly all the metallic elements. Such a scheme, in order to be of general applicability, must include a uniform procedure for obtaining the mineral in solution, from which the analytical groups are successively thrown down, and each group precipitate further separated into its constituent elements.

The method here adopted for preparing the solution is that of A. A. Noyes,[1] in which the solvents are applied in the following order:

(1) Nitric acid dissolves sulphides as well as most substances attacked by hydrochloric acid (but not the acid-earth compounds enumerated under (2)), while obviating the precipitation or volatilization of some elements as chlorides.

(2) The residue from (1) is treated with hydrofluoric acid, which decomposes silicates (except cyanite, andalusite, tourmaline, beryl, zircon, and topaz), tungstates, tantalates, niobates, and some titanium minerals.

(3) The residue from (2) is attacked with hydrochloric acid, then with *aqua regia*. This dissolves cinnabar, molybdenite, ferric oxides, manganese dioxide, lead sulphate, and gold.

(4) The residue from (3) is fused with sodium carbonate, bisulphate, or peroxide, according to its nature.

By means of this procedure the metallic constituents of any mineral mixture are dissolved and obtained in several solutions, occasionally in one. The various fractions may, as a rule, be combined before examination, or tested separately if desired; the hydrofluoric-acid solution of the acid-earth group, however, must always be examined by itself.

A comprehensive scheme of qualitative analysis, based on the work of Noyes, Browning, and others,[2] is given *below* in condensed tabular form. Table I contains the directions for effecting solution of the mineral; Tables II to VIII are devoted to the examination of the analytical groups, more particularly to the separation of the elements. For the sake of brevity, the confirmatory tests for the common metals have not been included in the tables. Directions for washing the precipitates have likewise been omitted in most cases.

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[1] *Chem. News*, 1906, 93, 146.

[2] For references to the original papers consult Browning's *Introduction to the Rarer Elements* (4th edition, 1917), pp. 207–226.

## TABLE I.*—OPENING UP.

Digest 1 g. of slimed mineral with 10 ml. $HNO_3$ (1 : 1) till action is over. Dilute with 20 ml. of hot $H_2O$, decant and filter.

$F^1$: evaporate to dryness, heat to 120° C. for 1 hour. Treat as, or combine with, final residue from $R^1$ after like treatment.

$R^1$: transfer to Pt dish, evaporate or decant water, digest with 5–10 ml. pure strong HF on water-bath. Evaporate twice to dryness with 5 ml. strong $HNO_3$, boil with 10 ml. $HNO_3$ (1 : 3). If solution is complete after HF or $HNO_3$ treatment, evaporate to dryness once more, heat to 120° C. for 1 hour. If complete solution has not taken place, evaporate to dryness, add 10 ml. strong $HNO_3$ and 1 g. pure $SiO_2$ (Note *a*). Cover, digest for three-quarters of an hour; evaporate to dryness, heat to 120° C. for an hour. Powder residue (and that from $F^1$), add 5 ml. $HNO_3$ (1 : 1), boil, dilute, decant and filter.

$R^2$: pour 5–10 ml. strong HF on to filter (rubber funnel), receive filtrate in Pt dish containing balance of residue. Heat 5 minutes, dilute, decant and filter into another Pt dish.

$F^2$: evaporate to dryness, take up with 40 ml. $H_2O$, add 4 ml. HCl (2 : 1 water), warm. If pptc. forms, filter it off and boil with $H_2O$; filter into HCl filtrate, test residue for Ag. Filtrate: Table IV.

$F^3$: Table II.

$R^3$: boil gently in porcelain with 15 ml. strong HCl, dilute and filter, digest residue with *aqua regia*, dilute, filter into HCl solution. Dry or ignite residue.

$F^4$: evaporate to dryness, take up with HCl (1 : 4), filter.

$R^5$: digest with $NH_4OH$, filter.

$F^5$: Table IV.

$F^6$: test for Ag.

$R^6$: boil with $CH_3CO_2NH_4$, filter.

$R^7$: $SrSO_4$ or $BaSO_4$. Fuse with $Na_2CO_3$; see Table VII, $P^1$.

$F^7$: test for Pb.

$R^4$: fuse with (*a*) $Na_2CO_3$, (*b*) $NaHSO_4$, or (*c*) $Na_2O_2$; *below*.

(*a*) If non-metallic and light-coloured, or in doubtful cases, fuse with $Na_2CO_3$, leach, filter.

$R^8$: digest with HCl, filter.

$R^9$: see (*b*).

$F^9$: see Table IV.

$F^8$: evaporate with HCl, heat to 120° C., digest with HCl (1 : 1), filter.

$R^{10}$: see $R^2$.

$F^{10}$: see Table IV.

(*b*) If non-metallic and light-coloured, and thought to consist of oxides, fluorides, or phosphates, fuse with bisulphate in silica crucible, leach, filter.

$R^{11}$: treat as $R^2$, filter.

$F^{11}$: Table IV.

$R^{12}$: if $BaSO_4$ or $SrSO_4$, see $R^7$; if $SiO_2$ or silicates, see (*a*); if $SnO_2$, see (*c*).

$F^{12}$: Table II.

(*c*) If metallic, or non-metallic and dark, fuse with $Na_2O_2$ in Ni crucible, leach, acidify with HCl, evaporate to dryness, heat to 120° C. for an hour, boil with dilute HCl, filter (see Note *b*).

$R^{13}$: dissolve in HF; see Table II.

$F^{13}$: examine separately (Table IV *et seq.*). Reject nickel filtrate.

*Note a* (to $R^1$).—The silica used must be pure and free from residue. It is prepared from water-glass diluted with 3 volumes of water and treated with a slight excess of hydrochloric acid; the clear liquid is decanted off, and the precipitate boiled 2 to 3 times with water and dried. The dry residue is boiled 2 to 3 times with strong hydrochloric acid, washed free from acid, dried, and ignited.

*Note b* (to $R^4$ (*c*)).—If from the metallic appearance of the residue the presence of platinum metals or osmiridium is inferred, proceed as in Table III.

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* In the tables given in this and the following section, P denotes precipitate; R, residue; F, filtrate; S, solution; D, distillate; L, loss.

## TABLE II.—ACID-EARTH GROUP.

<table>
<tr><td colspan="6">The solution ($F^3$, $F^{12}$, or $R^{10}$, $R^{13}$ dissolved in HF; see Table I) is ppted. with $H_2S$ (rubber tube). Filter through rubber funnel.</td></tr>
<tr><td colspan="3">$P^1$ (may contain Sb, Mo, As, Bi): digest with $(NH_4)_2S$, filter.</td><td colspan="3">$F^1$ (Ta, Nb, Ti, Zr, Hf, W, Si): evaporate to fumes with $H_2SO_4$; add $NH_4OH$ and $(NH_4)_2S$, filter (Note *a*).</td></tr>
<tr><td>$R^2$: test for Bi.</td><td colspan="2">$F^2$: add to $F^3$.</td><td>$F^3$: add $F^2$, acidify with $H_2SO_4$, filter.</td><td colspan="2">$P^3$: ignite, fuse with bisulphate, extract melt with acid tannin solution (Note *b*).</td></tr>
<tr><td colspan="2" rowspan="2">$F^5$: evaporate to fumes, dilute, add HCl + Zn: blue ppte. = W.</td><td colspan="2">$P^5$: dry, heat in $H_2S$ current.</td><td rowspan="2">$R^4$: test for Nb and Ta as described in **XVIII,** § VI.</td><td rowspan="2">$F^4$: destroy tannin by evaporation with sulphuric acid, test diluted solution for Ti and Zr as in Table V, $S^8$.</td></tr>
<tr><td>Sublimate$^6$: test for As.</td><td>$R^6$: boil with strong HCl, dilute, filter.</td></tr>
<tr><td>$F^7$: test for Sn and Sb.</td><td colspan="5">$R^7$: boil with $HNO_3$, evaporate to fumes with $H_2SO_4$, cool, add three volumes of $H_2O$, filter.</td></tr>
<tr><td colspan="3">$F^8$: add Zn + KCNS. Red colour = Mo.</td><td colspan="3">$R^8$: add Zn + HCl. Blue ppte. = W.</td></tr>
</table>

*Note a* (to $F^1$).—If much W and/or Mo are present, the ppte. is redissolved in HF, the solution evaporated with $H_2SO_4$, and the pption. with $NH_4OH$ and $(NH_4)_2S$ repeated. Combine filtrates.

*Note b* (to $P^3$).—Pyrosulphate-tannin method: for particulars, see **XVIII,** § VI.

*Note c* (to $F^1$).—Hf occurs in all Zr minerals and affords the same reactions as Zr (see **XIV**).

## TABLE III.—PLATINUM GROUP.

<table>
<tr><td colspan="5">Fuse $R^4$, (*c*) (Table I) with $Na_2O_2$ in nickel crucible. Leach with $H_2O$, transfer to distillation flask, acidify with HCl, distil with $NaClO_3$, then $NaBrO_3$,* collect distillate in cooled NaOH.</td></tr>
<tr><td colspan="2">$D^1$: if yellow or brown, return to empty distillation flask, acidify with HCl, again distil into NaOH.</td><td colspan="3">$S^1$: neutralize with $NaHCO_3$, boil, filter.</td></tr>
<tr><td>$D^2$: yellow = Os.†</td><td>$S^2$: red-brown = Ru.‡</td><td colspan="2">$P^3$: dissolve in HCl and enough $SO_2$ to discharge dark blue colour; evaporate with a few drops of $HNO_3$, ppte. hot concentrated solution with $NH_4Cl$ and $NaClO_3$. Allow to cool, filter.</td><td>$F^3$: add NaOH and $N_2H_4$, boil. Black ppte. = Pt. Confirm by solution in *aqua regia* and pption. with $NH_4Cl$.§</td></tr>
<tr><td colspan="3">$P^4$ = Ir, Pd, (Rh). Boil with 0·5 N-HCl, again evaporate, filter.</td><td colspan="2" rowspan="2">$F^4$: add filtrate from $F^5$. Ppte. with Zn, collect ppte., extract it with HCl, then with $NH_4OH + (NH_4)_2S_2O_8$ to dissolve Cu, Ag. Ignite black residue, reduce, ignite with NaCl in $Cl_2$ current,** dissolve melt in $H_2O$. Pink solution = Rh.</td></tr>
<tr><td>$P^5$: black, crystalline = Ir.‖</td><td colspan="2">$F^5$: ppte. with dimethylglyoxime: yellow ppte. = Pd.¶ Filter, add F to $F^4$.</td></tr>
</table>

* See **XXIV,** § III (44).

† *Ibid.*, § VI (80).

‡ *Ibid.*, § VI (81).

§ *Ibid.*, § VI (84).

‖ *Ibid.*, § VI (83).

¶ *Ibid.*, § III (46, *a*).

** *Ibid.*, § VI (82, *a*).

### Table IV.—Hydrogen Sulphide Group.

(Germanium and rarer platinum metals omitted. For germanium a separate test should be made (**XVI**, § V); for platinum metals, see preceding table.)

<table>
<tr><td colspan="9">Precipitate the solutions referred to this table in Table I, separately or combined, with $H_2S$. Filter, again pass $H_2S$ through filtrate; if ppte. forms, add it to the first.</td></tr>
<tr><td colspan="6">$P^1$: digest, hot, with $(NH_4)_2S$. Filter.</td><td colspan="3">$F^1$: see Table V.</td></tr>
<tr><td colspan="4">$R^2$: boil with $HNO_3$ (1 : 1); filter.</td><td colspan="5">$F^2$: ppte. with dilute HCl, filter, reject filtrate. Boil ppte. with strong HCl; filter.</td></tr>
<tr><td colspan="2">$F^3$: test for Pb, Bi, Cu, Cd.</td><td colspan="2">$R^3$: digest with $Br_2$, filter.</td><td colspan="4" rowspan="2">$R^7$: dissolve in $HCl + KClO_3$, evaporate, take up with a little $H_2O$; filter.</td><td rowspan="2">$F^7$: test for Sb, Sn.</td></tr>
<tr><td colspan="3">$F^4$: add KCl, evaporate to low volume, let stand, filter.</td><td>$R^4 = SnO_2$.</td></tr>
<tr><td>$P^5 = K_2PtCl_6$.</td><td colspan="3">$F^5$: add NaOH and $C_2O_4H_2$, boil, filter.</td><td>$P^8 = K_2PtCl_6$.</td><td colspan="4">$F^8$: add $NH_4Cl$, $NH_4OH$, and Mg mixture. Let stand overnight, filter.</td></tr>
<tr><td colspan="3">$F^6$: test for Hg.</td><td>$P^6 = Au$.</td><td colspan="3">$F^9$: boil with excess of $C_2O_4H_2$. Filter.</td><td colspan="2">$P^9$: test for As.</td></tr>
<tr><td colspan="8">$F^{10}$: evaporate nearly to dryness, add 10 ml. of strong HCl, reduce in the cold with 0·2 g. $Na_2SO_3$; let stand, filter.</td><td>$P^{10} = Au$.</td></tr>
<tr><td colspan="3">$P^{11}$: red, soluble in $KCN = Se$.</td><td colspan="6">$F^{11}$: add equal volume of $H_2O$ and a little KI and $Na_2SO_3$. Filter.</td></tr>
<tr><td colspan="5">$F^{12}$: boil to expel $SO_2$, add KCNS + Zn: red colour = Mo.</td><td colspan="4">$P^{12}$: black, soluble in $H_2SO_4$ with red colour = Te.</td></tr>
</table>

### Table V.—Ammonia-Ammonium Sulphide Group.

(Exclusive of Indium and Gallium, *q.v.*)

<table>
<tr><td colspan="5">To $F^1$, Table IV, add 5 g. $NH_4Cl$ and a slight excess of $NH_4OH$; pass $H_2S$. Filter.</td></tr>
<tr><td colspan="3" rowspan="2">$P^1$: add $P^2$, dissolve in HCl, boil, add $HNO_3$, evaporate, add $H_2O$, ppte. with $C_2O_4H_2$ (see **XII**, § VI). Filter.</td><td colspan="2">$F^1$: acidify with $CH_3CO_2H$, boil, filter.</td></tr>
<tr><td>$P^2$ (if any): add to $P^1$.</td><td>$F^2$: see Table VII.</td></tr>
<tr><td colspan="2">$P^3$: see Table VI.</td><td colspan="3">$F^3$: evaporate to fumes with $H_2SO_4$, dilute. If any white crystalline ppte. remains, fuse it with $Na_2CO_3$, and proceed as in Table VII, $P^1$. To filtrate, or original $F^3$, add NaOH, $Na_2O_2$, $Na_2CO_3$; boil and filter.</td></tr>
<tr><td colspan="3">$P^4$: dissolve in HCl, destroy HCl with $HNO_3$, boil with $KClO_3$. Filter.</td><td colspan="2">$F^4$: add faint excess of $HNO_3$, dilute to 100 ml., treat with excess of 2–3 g. of $NaHCO_3$, heat 20–30 minutes in a pressure bottle. Filter.</td></tr>
<tr><td>$P^5 = MnO_2$.</td><td colspan="2">$F^5$: test for $P_2O_5$; if present, test first for Fe, then add sufficiency of $FeCl_3$, neutralize with $Na_2CO_3$, add 2 g. $CH_3CO_2Na$, boil, filter.</td><td>$P^{11}$: dissolve in HCl, add $NH_4OH$, filter.</td><td>$F^{11}$: neutralize with $HNO_3$, add $Pb(CH_3CO_2)_2$, filter.</td></tr>
</table>

(Table continued on opposite page.)

## TABLE V.—AMMONIA-AMMONIUM SULPHIDE GROUP—*Continued.*

<table>
<tr><td colspan="2">$F^6$: pass $H_2S$, filter.</td><td colspan="4">$P^6$: dissolve in HCl (1 : 1), extract with ether.</td><td rowspan="2">$P^{12}$: ignite, fuse with $Na_2CO_3$, leach melt with $H_2O$.</td><td rowspan="2">$F^{12}$: test for Zn.</td><td rowspan="2">$F^{14}$: ppte. with $H_2S$, filter, reject PbS; to filtrate add $Br_2$, boil, neutralize with $NH_4OH$; add $CH_3CO_2H$ and $Na_2HPO_4$. Filter.</td><td rowspan="2">$P^{14} = PbCrO_4$.</td></tr>
<tr><td rowspan="2">$P^7$: test for Co, Ni, Zn.</td><td rowspan="2">$F^7$: see Table VII.</td><td colspan="2">$S^8$: evaporate with $H_2SO_4$, adjust acidity to 1 per cent., add $H_2O_2 + Na_2HPO_4$. Filter.</td><td colspan="2">Ether$^8$: evaporate, take up with $H_2SO_4$, add KI and $SO_2$, filter.</td></tr>
<tr><td>$F^{10}$: yellow to orange = Ti.</td><td>$P^{10}$ = Zr (Hf) phosphate. For confirmatory test, see **XIV**, § V.</td><td>$F^9$ = Fe.</td><td>$P^9$: yellow = Tl.</td><td>$F^{13}$: test for Al.</td><td>$R^{13}$: test for Be (**VII**, § VI).</td><td>$P^{15}$: yellow = U.</td><td>$F^{15}$: add $NH_4OH$, pass $H_2S$: red, pink, or violet solution = V.</td></tr>
</table>

## TABLE VI.—RARE-EARTH GROUP.

<table>
<tr><td colspan="5">Ignite $P^3$ (Table V) at 600° C., mix residue with strong $H_2SO_4$ to thick paste, heat gently at first, then to 500° C. until fumes of $H_2SO_4$ cease to be evolved. Dissolve in cold water, saturate solution with $Na_2SO_4$, let settle, filter, wash with saturated $Na_2SO_4$ solution.</td></tr>
<tr><td colspan="2">$P^1$: digest with NaOH, filter, reject filtrate. Open filter, dry in oven at 100° C., stirring ppte. to promote oxidation. Ppte. turns yellow if Ce is present. Dissolve dry ppte. in cold $HNO_3$ (1 : 1): orange solution proves presence of Ce. Dilute with 5 vols. of $H_2O$, add $KIO_3$ until pption. is complete; filter.</td><td colspan="3">$F^1$: add $CH_3CO_2Na$ and a little sodium alizarin-3-sulphonate; boil, filter.</td></tr>
<tr><td rowspan="2">$P^2$: boil with HCl and $SO_2$, then with excess of NaOH. Filter, wash thoroughly, dissolve ppte. in $HNO_3$ and a few drops of $H_2O_2$. Evaporate to dryness, take up with $NH_4NO_3$ solution, add $H_2O_2$; white ppte. = Th.</td><td rowspan="2">$F^2$: add excess NaOH, boil, filter, wash, ignite. Brown residue = Nd + Pr. In minerals, Nd and Pr always occur in association with La.</td><td colspan="2">$P^3$: violet. Dissolve in HCl, boil with $NH_4F$.</td><td rowspan="2">$F^3$: ppte. with $C_2O_4H_2$. Crystalline ppte. = yttria earths. These always occur in association. Identification of individual earths requires spectroscopic tests.</td></tr>
<tr><td>$P^4$: gelatinous, white = Th.</td><td>$F^4$: evaporate to small volume, add $Co(NH_3)_6(NO_3)_3$; crystalline ppte. of $Co(NH_3)_6ScF_6$ = Sc.</td></tr>
</table>

### TABLE VII.—ALKALINE-EARTH GROUP.

<table>
<tr><td colspan="3">To $F^2$ or to $F^7$, Table V, add $(NH_4)_2CO_3$ solution (Note *a*). Boil, filter.</td></tr>
<tr><td colspan="2">$P^1$: dissolve ppte., and the residue from leaching the soda fusion of any residues obtained in $R^7$, $R^{12}$, Table I, and $F^3$, Table V, in $HNO_3$. Evaporate to complete dryness, heat to 140° C. Extract with ether-alcohol (1 : 1), filter.</td><td>$F^1$: Table VIII.</td></tr>
<tr><td rowspan="2">$F^2$: evaporate to dryness, test residue for CaO.</td><td colspan="2">$R^2$: dissolve in $H_2O$, add a few drops of $CH_3CO_2H$ and $K_2CrO_4$. Filter.</td></tr>
<tr><td>$F^3$: concentrate, add $NH_4OH + (NH_4)_2CO_3$, boil, filter, test ppte. for Sr.</td><td>$P^3$: yellow = Ba.</td></tr>
</table>

*Note a.*—$F^2$ and $F^7$, Table V, should not be mixed, because $F^7$ contains sodium.

### TABLE VIII.—ALKALI GROUP.

<table>
<tr><td colspan="5">Evaporate $F^1$, Table VII, to dryness. Ignite gently to expel $NH_4$ salts. Add solution of 1 g. $C_2O_4H_2$, evaporate to dryness, ignite. Extract with hot $H_2O$, filter.</td></tr>
<tr><td>$R^1$: test for Mg.</td><td colspan="4">$F^1$: evaporate to dryness with HCl, extract with amyl alcohol, filter.</td></tr>
<tr><td colspan="3">$R^2$: add a few drops of $H_2O$, excess of $H_2PtCl_6$, let stand, filter.</td><td colspan="2">$F^2$: evaporate to dryness, test residue spectroscopically for Li.</td></tr>
<tr><td colspan="2">$P^3$: test spectroscopically for Rb, Cs.</td><td colspan="3">$F^3$: add equal volume of alcohol, filter, wash with 50 per cent. alcohol.</td></tr>
<tr><td colspan="4">$F^4$: Na (see Note *a*). Add a few drops of 1 per cent. alcoholic $H_2SO_4$: crystalline ppte. of $Na_2SO_4$. If no ppte. is formed, saturate solution with HCl gas: crystalline ppte. of NaCl.</td><td>$P^4$: test spectroscopically for K.</td></tr>
</table>

*Note a* (to $F^4$).—Not applicable to solutions resulting from the fusion of $R^4$, Table I, with $Na_2CO_3$, $NaHSO_4$, or $Na_2O_2$, nor to one derived from $F^7$, Table V.

## IV.—COMPLETE CHEMICAL ANALYSIS.[1]

IN addition to the descriptions of individual analyses given in the succeeding sections, it is thought useful here to present some general information on the subject of complete analysis, including the resolution of group precipitates of greater or lesser complexity into their constituents. Since a general scheme taking into account nearly all the elements would be far too involved, the directions here given refer only to the commoner ones, the separation of the rarer metals being discussed under their respective headings.

§ **I. Methods for Determining Elements.**—In assaying for single constituents, a fairly considerable amount of the element to be determined is generally obtained from a suitable quantity of ore; whereas in a complete analysis, the same portion is used for estimating a number of constituents, some being present in large, others in minute, quantity. The method of estimation used will often depend on the amount present; a colorimetric process is frequently adopted for small quantities (*e.g.* bismuth, titanium); sometimes it is preferable to weigh small precipitates rather than use a volumetric method (*e.g.* zinc, antimony). We may therefore distinguish between methods more suitable for moderate to large, and others for minute, quantities. Table IX shows the different methods of estimating some of the commoner elements by way of illustration; alumina, barium, silica, sulphur, and the alkalis have not been included, as they are practically always weighed.

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[1] This section is substantially an amplified reprint of a paper entitled "General Principles governing the Complete Analysis of Minerals and Ores," by W. R. Schoeller (*Analyst*, 1915, **40**, 90).

TABLE IX.

(G., gravimetric, V., volumetric, E., electrolytic, C., colorimetric, determination.)

| Element. | Moderate to Large Amounts. | Minute Quantities. |
|---|---|---|
| Antimony . | V. with permanganate, bromate, or iodine. E. as metal. | G. as $SbO_2$. |
| Arsenic . | V. with iodine or bromate. G. as $Mg_2As_2O_7$. | V. with iodine. |
| Bismuth . | G. as $Bi_2O_3$, or $BiPO_4$. | E. as metal. C. as $BiI_3$. |
| Calcium . | V. with permanganate. | G. as $CaSO_4$ or CaO. |
| Cobalt . | G. as $Co_2P_2O_7$. E. as metal. | G. as $CoSO_4$, or with nitroso-$\beta$-naphthol. |
| Copper . | V. with thiosulphate. E. as metal. G. as $Cu_2S$. | C. with ammonia or ferrocyanide. V. with thiosulphate. |
| Iron . . | V. with permanganate or dichromate. | G. as $Fe_2O_3$. C. with thiocyanate. |
| Lead . . | V. with thiosulphate. G. as $PbSO_4$ or $PbMoO_4$. | V. with thiosulphate. C. with $H_2S$. G. as $PbMoO_4$. |
| Magnesium | V. by alkalimetry. G. as $Mg_2P_2O_7$. | G. as $Mg_2P_2O_7$. |
| Manganese . | V. with permanganate, or oxalic acid and permanganate. | G. as $Mn_3O_4$. C. as $HMnO_4$. |
| Nickel . | E. as metal. V. with cyanide. | G. with dimethylglyoxime. V. with cyanide. |
| Phosphorus | V. by alkalimetry. G. as $Mg_2P_2O_7$. | G. as $PbMoO_4$. |
| Silver . | V. with thiocyanate or sodium chloride. E. as metal. G. as AgI or AgCl. | Scorification or crucible fusion. |
| Tin . . | V. with iodine. | V. with iodine. G. as $SnO_2$. |
| Zinc . . | V. with ferrocyanide or sodium sulphide. G. as $Zn_2P_2O_7$. | G. as ZnO. |

Speaking generally, a gravimetric process is preferable for small quantities to a volumetric where a certain excess of reagent is required to produce a good end-point, or still more to an indirect titration. Again, with still smaller quantities, the disadvantage of gravimetric methods lies in the fact that a small alteration in the weight of a crucible several thousand times heavier than its contents causes a considerable relative error in the determination, and if available a colorimetric process is to be preferred.

§ **II. Separation of Elements.**—For the quantitative separation of the common elements into groups the procedure is similar to that followed in qualitative analysis, while that of the elements from one another often requires more elaborate methods. A subdivision into groups and quantitative separation of the common elements is given *below* in an abridged form (Procedures 1 to 14).

## A. HYDROGEN SULPHIDE GROUP.

### First Case : Mercury is Absent.

Digest $H_2S$ precipitate, hot, with $Na_2S + NaOH$. Filter, wash with hot dilute $Na_2S$ solution.

Filtrate: Procedure 1. Residue: Procedure 2.

### *Procedure* 1.

Filtrate contains As, Sb, Sn, and a little Cu. Add $Na_2SO_3$ whilst boiling until yellow colour is discharged. Let settle, filter, wash with dilute $Na_2S$ solution.

$P^1 = CuS$. Add to Procedure 2.

$F^1$: add excess of $CH_3CO_2H$, pass $H_2S$, boil, let settle, filter, reject filtrate. Boil ppte. with strong $H_2SO_4$ until clear and sulphur has volatilized. Dilute with 1 vol. $H_2O$, cool, add 2·5 vol. strong HCl, pass $H_2S$, filter, wash with HCl (2·5 : 1 $H_2O$), then with 5 per cent. $H_2SO_4$ to displace HCl.

$P^2 = As_2S_3$. Dissolve in strong $H_2SO_4$, neutralize with $NaHCO_3$, titrate with $I_2$.

$F^2$: partly neutralize with $NH_4OH$, dilute, pass $H_2S$, filter, reject filtrate. Dissolve ppte. in HCl + $Br_2$, boil gently to expel $Br_2$, reduce hot with piano wire (about 20 minutes), filter, wash with 5 per cent. HCl.

$F^3$: reduce with soft iron nails, cool in running water in $CO_2$ current, titrate Sn with $I_2$.

$P^3$: dissolve in HCl + $Br_2$, evaporate $Br_2$, ppte. with $H_2S$, dissolve ppte. in strong $H_2SO_4$, add $H_2O$ and ⅛ vol. of strong HCl, titrate Sb with $KMnO_4$.

### *Procedure* 2.

Residue from $Na_2S$ treatment = Ag, Pb, Bi, Cu, Cd sulphides. Add $P^1$, Procedure 1. Dissolve in $HNO_3$ (1 : 3 $H_2O$), filter off sulphur, dilute to 200 ml., add 10 ml. of 10 per cent. KI, then 20 ml. of $HNO_3$ (1 : 1); boil till $I_2$ is expelled. Filter, wash with 5 per cent. $HNO_3$, then water.

$P^1 = AgI$. Dry, ignite, weigh.

$F^1$: evaporate excess of $HNO_3$, dilute, add slight excess of $Na_2CO_3$, then 1–2 g. KCN free from sulphur, digest hot, filter, wash.

$P^2$: dissolve in HCl, boil with 1–2 g. of very fine iron wire for 10–20 minutes; filter, wash with hot water.

$P^3$: dissolve in HCl + $Br_2$, boil, ppte. Bi with $H_2S$, filter, wash free from Fe. Dissolve $Bi_2S_3$ in $HNO_3$; determine Bi as $BiPO_4$.*

$F^3$: dilute, ppte. Pb with $H_2S$. Collect PbS, convert into and weigh as $PbSO_4$.

$F^2$: boil with slight excess of dilute $H_2SO_4$ till HCN is expelled. Ppte. boiling solution with $Na_2S_2O_3$, filter, wash with hot water.

$P^4 = Cu_2S$. Ignite, dissolve in $HNO_3$, apply iodine titration.

$F^4$: ppte. with $H_2S$; weigh as CdS or $Cd_2P_2O_7$.

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* W. R. Schoeller and D. A. Lambie, *Analyst*, 1937, **62**, 533.

## Second Case : Mercury is Present, Tin and Cadmium are Absent.

*Procedure* 3.

| | |
|---|---|
| Digest $H_2S$ ppte. with $Na_2S$, filter, and wash, as under First Case. | |
| $R^1$: see Procedure 2. | $F^1$: boil with excess of $NH_4Cl$; filter, wash with dilute $(NH_4)_2S$. |
| $P^2 = HgS$. Dissolve in $HCl + KClO_3$, expel $Cl_2$, ppte. with $SnCl_2$, weigh Hg. | $F^2$ : As, Sb, a little Cu. See Procedure 1. |

*Note.*—The possibility of the simultaneous occurrence of Hg, Sn, and Cd may be ruled out in ore analysis, since Cd is found only in Zn ores (which contain no Hg, and Sn only in traces). Tin ores are free from Hg, and *vice-versa.*

## Third Case : The Metals are Present partly as Acid-insoluble Compounds.

The action of the common acids on ores (and alloys) of the heavy metals may result in the formation of certain insoluble compounds (*e.g.* stannic acid, antimonic acid, lead sulphate, bismuth (tin) arsenate, silver chloride). In such cases, Biltz's method [1] is very useful.

*Procedure* 4.

Evaporate the unfiltered solution to dryness in a porcelain basin, rub the dry mass to a fine powder, stir in 10 g. of crystallized $Na_2S$ and 0·2 to 0·3 g. of sulphur; gently heat the covered basin so that the salt melts in its water of crystallization; fuse for 20 to 30 minutes with occasional stirring. Cool, dissolve melt in hot KCl solution, allow to settle, filter, wash with dilute $Na_2S$. Filtrate: see Procedure 1; residue: Procedure 2.

*Note a.*—Alternative procedure: In the case of antimonial and arsenical ores of the heavy metals, the finely powdered material is intimately mixed with 6 times its weight of a mixture of equal parts of sulphur and anhydrous $Na_2CO_3$, and heated in a covered porcelain crucible, gently at first, then strongly, until the excess of S has been driven off. The cold melt is extracted with hot water, and the solution filtered. Filtrate: see Procedure 1; residue: Procedure 2.

*Note b.*—Separate determination of heavy metals: see § V, *below.*

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[1] H. Biltz, *Zeitsch. anal. Chem.*, 1930, **81,** 81.

## B. AMMONIA-AMMONIUM SULPHIDE GROUP.

### *Procedure* 5.

*Note.*—For materials containing little titanium and phosphoric acid. If the ore is rich in titanium, consult **XIII,** § IX; if rich in phosphoric acid, apply Procedure 13, and in $F^3$ thereof determine all the metals according to Procedures 1 to 10.

Oxidize filtrate from $H_2S$ ppte. with $HNO_3$. To the hot solution add 5 g. of $NH_4Cl$, a slight excess of $NH_4OH$, and freshly prepared $(NH_4)_2S$. Allow to stand warm overnight, filter, wash with dilute $(NH_4)_2S$. If considerable quantities of alkaline earths are present, dissolve ppte. in HCl, repeat pption., combine filtrates.

$F^1$: apply Procedure 8 or 9.

$P^1$: dissolve in *aqua regia*, evaporate to dryness.

If Fe preponderates over Al, and Cr is absent, continue as *below*; if Al preponderates and Cr is present, apply Procedure 7.

Take up dry residue with 5 per cent. HCl, add 0·26 g. of $NH_4Cl$ for each 0·1 g. of Fe present. Evaporate to dryness on water-bath until the mass no longer smells of HCl. Take up with cold $H_2O$, add 2 to 4 g. of sodium acetate, dilute with 300 to 500 ml. of hot water, boil for a minute, filter, wash with hot water. With large quantities of Fe, Co, Ni, etc., dissolve ppte. in dilute HCl, repeat basic acetate pption., combine and concentrate filtrates.

$F^2$: see Procedure 6.

$P^2$: dissolve in dilute HCl, reppte. with dilute $NH_4OH$, add filter-pulp, collect, wash, and ignite ppte.; weigh as $(Fe_2O_3 + Al_2O_3 + TiO_2 + P_2O_5)$. Dissolve in strong HCl, fuse any small residue with bisulphate, add solution of melt to main filtrate, treat with tartaric acid, reduce ferric iron with $H_2S$, make ammoniacal, again pass $H_2S$, allow to settle, filter, wash with dilute $(NH_4)_2S$.

$P^3 = FeS$. Determine Fe volumetrically, or take $Fe_2O_3$ by difference.

$F^3$: evaporate with $HNO_3$ and $H_2SO_4$ to destroy tartaric acid. Dilute, filter, ppte. with $NH_4OH$, collect and ignite ppte.; weigh as $(Al_2O_3 + TiO_2 + P_2O_5)$. Fuse with $Na_2CO_3$, leach, filter; fuse residue with bisulphate. Acidify alkaline filtrate with $H_2SO_4$, combine solution with acid solution of bisulphate melt. Dilute to 250 ml. In 50 ml. (or less) determine $TiO_2$ colorimetrically. In 200 ml., determine $P_2O_5$ by molybdate method; $Al_2O_3$ by difference.

### *Procedure* 6.

Saturate $F^2$, Procedure 5, or $F^1$, Procedure 7, with $H_2S$, digest on water-bath till ppte. has settled. Filter, wash with $H_2S$-water containing a few drops of acetic acid and sodium acetate.

$F^1$: boil to expel $H_2S$, neutralize almost completely with $Na_2CO_3$, boil, add 20 ml. $Br_2$-water and 1 to 2 g. sodium acetate. Boil to expel $Br_2$, collect $MnO_2$, dissolve in $C_2O_4H_2$, titrate back with $KMnO_4$.

$P^1$: dissolve in $HCl + Br_2$, evaporate off excess of $Br_2$, carefully neutralize with $NH_4OH$, add 8 to 10 drops 2N-HCl and 2 g. $(NH_4)_2SO_4$ per 100 ml. bulk. Heat to 50° C., saturate with $H_2S$, allow to settle, filter, wash with 2 per cent. $(NH_4)_2SO_4$ solution saturated with $H_2S$. If much Co and/or Ni is present, the ppted. ZnS may not be white. If so, collect ppte., dissolve in $HCl + Br_2$, repeat $H_2S$ pption., combine filtrates.

$F^2$: boil to expel $H_2S$, add excess of sodium acetate and alcoholic dimethylglyoxime solution. Filter.

$P^2 = ZnS$. Dissolve and titrate, or ignite to ZnO.

$P^3$ = nickel. If small, ignite to NiO. If large, evaporate with $HCl + KClO_3$, treat $NiCl_2$ solution with $NH_4Cl$ and slight excess of $NH_4OH$, titrate with KCN.

$F^3$: evaporate to dryness with HCl and $KClO_3$ to destroy excess of reagent; ppte. Co as $CoNH_4PO_4$, weigh as $Co_2P_2O_7$.

### *Procedure* 7.

<table>
<tr><td colspan="4">Dissolve $P^1$, Procedure 5, in *aqua regia*, evaporate to dryness, take up with dilute HCl. Add 10 g. of $NH_4Cl$, neutralize approximately with $NH_4OH$, dilute to 200–300 ml., heat to boiling, add slight excess of 10 per cent. hexamethylenetetramine solution. Allow to settle, filter, wash with hot water. If large quantities of metals are present, dissolve ppte. in dilute HCl, repeat pption., combine filtrates.</td></tr>
<tr><td colspan="2">$F^1$: evaporate to dryness with excess of HCl. Take up with hot water, add a little sodium acetate and a few drops of acetic acid; apply Procedure 6.</td><td colspan="2">$P^1 = Al_2O_3$, $Cr_2O_3$, $Fe_2O_3$, $TiO_2$, $P_2O_5$. Ignite to constant weight. Fuse with $Na_2CO_3$ and a little $KNO_3$. Leach with hot water, filter.</td></tr>
<tr><td colspan="2">$F^2 = Al_2O_3$, $CrO_3$, $P_2O_5$. Treat with excess of $NH_4Cl$, digest hot, filter.</td><td colspan="2">$R^2 = Fe_2O_3$, $TiO_2$. Fuse with bisulphate, dissolve in tartaric acid, pass $H_2S$, add $NH_4OH$, let settle, filter.</td></tr>
<tr><td>$P^3$ $Al_2O_3$, $P_2O_5$. Dissolve in $HNO_3$, determine $P_2O_5$ by molybdate; $Al_2O_3$ by difference.</td><td>$F^3$: acidify, titrate $CrO_3$ with KI and $Na_2S_2O_3$.</td><td>$P^4 = FeS$. Dissolve and titrate, or convert to $Fe_2O_3$.</td><td>$F^4$: boil to destroy $(NH_4)_2S$, ppte. $TiO_2$ with tannin (**XIII**, § IV, *c*).</td></tr>
</table>

## C. ALKALINE EARTHS.

## First Case : Barium, Strontium, and Alkalis are Absent.

### *Procedure* 8.

<table>
<tr><td colspan="2">The concentrated filtrate $F^1$, Procedure 5, is treated with 5 g. $NH_4Cl$ if not already present, made ammoniacal, and pptd. with $(NH_4)_2C_2O_4$. If much Mg is present, redissolve and repeat pption.; combine filtrates.</td></tr>
<tr><td>$P^1 = CaC_2O_4$. Titrate with $KMnO_4$, or weigh as CaO or $CaSO_4$.</td><td>$F^1$: concentrate, digest at a gentle heat with strong $HNO_3$ (3 times the weight of $NH_4Cl$ present), evaporate nearly to dryness, take up with 2 ml. of HCl, add slight excess of $NaNH_4HPO_4$, make ammoniacal; add $\frac{1}{10}$ the volume of strong $NH_4OH$. Filter next day, wash ppte. with 10 per cent. $NH_4OH$, ignite, and weigh as $Mg_2P_2O_7$; or wash with 50 per cent. alcohol and titrate with N/5 acid.</td></tr>
</table>

## Second Case : All the Alkaline Earths and Alkalis are Present.

### *Procedure* 9.

The concentrated filtrate F$^1$, Procedure 5, is treated with 5 g. of $NH_4Cl$ if not already present, made ammoniacal, and ppted. with $(NH_4)_2CO_3$. Filter and wash with hot water.

P$^1$: dissolve in $HNO_3$, add solution from P$^4$. Evaporate to dryness in a flask, heat residue for 1 to 2 hours at 140° C. in a current of warm air. Treat dry residue with ten times its weight of absolute alcohol in a stoppered flask, allow to stand 2 hours. Add equal volume of ether, set stoppered flask aside overnight. Filter, wash with ether-alcohol (1 : 1).

F$^1$: add 3 to 4 drops dilute $H_2SO_4$ and 1 ml. $(NH_4)_2C_2O_4$, let stand overnight, filter.

| | |
|---|---|
| P$^4$: ignite, fuse with $Na_2CO_3$, dissolve washed residue in $HNO_3$, add to P$^1$. | F$^4$: apply Procedures 10 or 11. |

F$^2$: evaporate to dryness, take up with water, ppte. CaO as oxalate.

R$^2$: dissolve in $H_2O$ (300 ml. per g. of mixture), boil, add 6 drops of $CH_3CO_2H$ and 10 ml. of 10 per cent. $(NH_4)_2CrO_4$. Let stand 1 hour. Filter, wash by decantation with very dilute $(NH_4)_2CrO_4$, then hot $H_2O$. Rinse back ppte., dissolve in little dilute $HNO_3$, dilute to 200 ml., boil, add slowly 5 ml. of $CH_3CO_2NH_4$ and enough $(NH_4)_2CrO_4$ to neutralize $CH_3CO_2H$ (absence of smell). Let stand 1 hour, filter, wash with $H_2O$. Combine filtrates.

| | |
|---|---|
| P$^3$: dry, ignite gently, weigh $BaCrO_4$. | F$^3$: concentrate, add excess of dilute $H_2SO_4$ and an equal volume of alcohol. Let stand overnight, filter, wash with 50 per cent. alcohol. Ignite, weigh $SrSO_4$. |

## D. MAGNESIA AND ALKALIS.

### *Procedure* 10.

(If sulphates are present, apply Procedure 11.)

Evaporate filtrate F$^4$, Procedure 9, to dryness in platinum. Gently ignite residue, take up with a little $H_2O$, add 1 g. $C_2O_4H_2$, evaporate to dryness, ignite gently. Extract with a little $H_2O$, filter, wash.

| | |
|---|---|
| R$^1$ = MgO. Dry, ignite, weigh. | F$^1$: add small excess of HCl, evaporate in platinum, ignite gently, weigh KCl + NaCl containing a little $MgCl_2$. Take up with a little $H_2O$ and 1 drop HCl, add excess of $H_2PtCl_6$, evaporate to dryness, take up with strong alcohol, filter, wash with alcohol. |

| | |
|---|---|
| P$^2$: dry, separate from filter, rinse paper with hot water, evaporate washings to dryness, add ppte., heat to 160° C., weigh $K_2PtCl_6$. Calculate KCl. | F$^2$: evaporate to dryness, take up with very dilute HCl, ppte. Pt with $H_2S$ (hot), filter, evaporate filtrate to small bulk, ppte. small quantity of Mg as $MgNH_4PO_4$. Calculate $MgCl_2$. NaCl is obtained by difference. |

### *Procedure* 11.

The filtrate $F^4$, Procedure 9, is acidified with HCl and treated with sufficient $BaCl_2$ to ppte. sulphates, followed by $NH_4OH$ and $(NH_4)_2CO_3$ to remove excess of $BaCl_2$. Filter, reject pptc., evaporate filtrate to dryness, gently ignite residue, take up with a few drops of HCl, add $Ba(OH)_2$ till slightly alkaline, boil, filter, wash with hot water.

$P^1$: dissolve in slight excess of HCl, ppte. hot with $H_2SO_4$, filter off $BaSO_4$, ppte. MgO in filtrate as $MgNH_4PO_4$.

$F^1$: ppte. with $NH_4OH + (NH_4)_2CO_3$, filter, evaporate filtrate to dryness, gently ignite residue, take up with a little $H_2O$, repeat pption. to remove last traces of Ba. Evaporate filtrate, moisten residue with HCl, again evaporate, ignite residue gently, weigh KCl + NaCl + small amount of $MgCl_2$. Apply Procedure 10, $F^1$.

## E. Common Acid Radicals.

These are assumed to have been converted into sodium salts by fusion with sodium carbonate.

### First Case : Silica, Sulphuric Acid (as Barytes), Alumina, and Small Amounts of Titanic and Phosphoric Acids Present. Halogens and Boric Acid Absent.

### *Procedure* 12.

Digest $Na_2CO_3$ melt with $H_2O$, acidify with HCl, evaporate to complete dryness on water-bath. Digest residue with strong HCl for 10 minutes. Add hot $H_2O$, filter by decantation, again pour decanted solution through filter, wash with acidulated water.

$R^1$: add $R^4$. Ignite wet in platinum, weigh. Evaporate with $HF + H_2SO_4$, ignite with $(NH_4)_2CO_3$, weigh again.

$L^2 = SiO_2$.

$R^2$: fuse with $NaHSO_4$, leach with cold water. Filter, wash.

$R^3 = BaSO_4$. Ignite, weigh.

$F^3$: add to $F^4$.

$F^1$: evaporate to complete dryness on water-bath. Take up with dilute HCl, filter, wash.

$R^4$ = 2nd $SiO_2$. Add to $R^1$.

$F^4$: pass $H_2S$, filter, reject ppte. Oxidize filtrate with $HNO_3$, add $F^3$, ppte. with $NH_4Cl + NH_4OH$, dissolve, reppte., ignite, weigh, etc., as under Procedure 5, $P^2$ *et seq.*

## Second Case : Phosphoric and Arsenic Acids, Fluorine, Chlorine, Silica, and Titanic Acid (*e.g.* in Apatite-group Minerals).

*Procedure* 13.

(*Note.*—The fluorine determination is preferably carried out in a separate portion.)

<table>
<tr><td colspan="7">Extract $Na_2CO_3$ melt with hot water, filter, wash with 2 per cent. $Na_2CO_3$.</td></tr>
<tr><td colspan="3">$R^1$: dissolve in HCl in porcelain basin, evaporate to dryness, take up with HCl, filter.</td><td colspan="4">$F^1$: add 10 g. of solid $(NH_4)_2CO_3$, let stand at 40° C. overnight. Filter, wash with $(NH_4)_2CO_3$-water.</td></tr>
<tr><td>$R^2$ = 1st $SiO_2$. Add to $R^3$.</td><td colspan="2">$F^2$: evaporate to dryness, take up with HCl, filter.</td><td>$P^5$: add to $P^6$.</td><td colspan="3">$F^5$: add a few ml. of ammoniacal ZnO solution, boil till all $NH_3$ is expelled. Filter, wash.</td></tr>
<tr><td rowspan="4">$F^3$: pass $H_2S$, filter, reject Pt ppte.; treat filtrate with $NH_4OH$, dissolve ppte. in $H_2SO_4$, and continue as under $P^2$ <em>et seq.</em>, Procedure 5, to obtain $TiO_2$; add $R^4$, fuse with $NaHSO_4$, determine $TiO_2$ colorimetrically. (See Note <em>a.</em>)</td><td colspan="2">$R^3$ = 2nd $SiO_2$. Add $R^2$, $R^7$, and $R^8$. Ignite and weigh. Treat with HF + $H_2SO_4$, ignite with $(NH_4)_2CO_3$, weigh again.</td><td colspan="2">$P^6$: add $P^5$; evaporate to dryness with HCl, take up with dilute HCl, filter, wash.</td><td colspan="2">$F^6$: add phenolphthalein, cautiously neutralize with $HNO_3$; add $AgNO_3$ solution, filter, wash with minimum of cold water.</td></tr>
<tr><td>$L^4$ = $SiO_2$.</td><td>$R^4$: add to $TiO_2$ from $F^3$.</td><td>$R^7$: add to $R^3$.</td><td>$F^7$: evaporate again to dryness with HCl, take up with dilute HCl, filter, wash.</td><td rowspan="2">$F^9$: contains F. See Note <em>b.</em></td><td rowspan="2">$P^9$: extract with dilute $HNO_3$, filter, wash.</td></tr>
<tr><td colspan="2" rowspan="2"></td><td>$R^8$: add to $R^3$.</td><td>$F^8$: add to solution from $F^{10}$.</td></tr>
<tr><td colspan="2">$F^{10}$: ppte. with HCl, filter, wash, reject ppte., add $F^8$, ppte. with $H_2S$. Filter.</td><td colspan="2">$R^{10}$: AgCl. Ignite, weigh.</td></tr>
<tr><td colspan="3">$P^{11}$: determine $As_2O_5$.</td><td colspan="4">$F^{11}$: determine $P_2O_5$. (See Note <em>a.</em>)</td></tr>
</table>

*Note a* (to $F^3$).—If the metals are to be determined in the same portion, this filtrate is examined according to Procedures 1 to 10: $F^{11}$ should then be examined for Al as well as for $P_2O_5$.

*Note b.*—Treatment of $F^9$: Ppte. Ag with NaCl, filter, reject ppte. Add 1 ml. of 2N-$Na_2CO_3$ solution to filtrate, boil, add excess of $CaCl_2$ solution, filter, wash with hot water. Transfer dried ppte. to Pt dish, add filter-ash. Ignite, digest with dilute $CH_3CO_2H$, take to dryness, extract with $H_2O$, filter, wash, dry; separate ppte. from paper, ignite, weigh $CaF_2$.

### Third Case : Silica, Fluorine, Boric Acid.

*Procedure* 14.

(*a*) *First Portion :* Boron.—The solution of the $Na_2CO_3$ melt is faintly acidified to litmus with $CH_3CO_2H$. Add slight excess of $Ca(CH_3CO_2)_2$, distil the whole with pure $CH_3OH$ several times into a receiver containing a known weight of pure CaO previously slaked. The distillate is evaporated at very low temperature, the residue gently heated, transferred to a tared crucible with water, and ignited to constant weight. The increase in weight over CaO is $B_2O_3$.

(*b*) *Second Portion :* Silica and fluorine.—Apply Procedure 13, obtaining $SiO_2$ in $R^1$, $P^5$, and $P^6$; in this case the three precipitates are mixed and treated as described under $R^1$. For fluorine, the filtrate from the ammoniacal ZnO treatment is treated with 1 ml. of 2N-$Na_2CO_3$ solution, etc., as described in Note *b*, Procedure 13.

§ **III. Other Methods of Separation.**—Besides the above group separations, a number of shorter methods can be applied where only two elements have to be separated, or where it is not intended to estimate every constituent in the same portion. Two elements belonging to different groups need not necessarily be separated by the group reagent. As with the actual estimation, the best method for separation will frequently depend on the quantities present; in making one's choice one should, if possible, aim at leaving or obtaining the predominant element in solution and at precipitating the subordinate, so as to avoid or minimize occlusion and coprecipitation and the washing of bulky precipitates; or at producing a crystalline or heavy, rather than an amorphous or voluminous, precipitate. Table X is intended to illustrate this principle. The term "converse" may be applied to two methods if they can be used alternatively for the separation of two elements, subject to one being predominant or subordinate in quantity. To facilitate the use of the table, the number of each method is followed by that of its converse in brackets. Some separations are not perfect because a small quantity of the predominant element is carried down with the precipitated subordinate; in this case the precipitate is subjected to a second treatment by the same or the converse method, which is easily done on account of its small bulk. Thus in 18 (Table X) the insoluble tin oxide takes down a small quantity of lead as stannate, and is treated as in 13: this is far better than extracting tin from lead sulphide by sodium sulphide. Most of these methods can be used for separating three or more elements (compare 6 and 11; 18 and 23; 41 and 42; 37 and 39).

§ **IV. Separation into Insoluble Residue and Soluble Fraction.**—The usual acid treatment of minerals, etc. commonly results in a solution of the metals and an insoluble residue. Where the latter contains no compounds of heavy metals, such as oxides of tin or antimony, chromite, tungstic acid, silver chloride, etc., it consists of the insoluble part of the gangue, chiefly silica, barium sulphate, or silicates.[1] The silica was either originally present as quartz or liberated from a silicate by the acid treatment. Most silicates and rocks, though termed insoluble, yield a small soluble fraction,

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[1] For the complete analysis of silicate rocks consult Hillebrand and Lundell, *op. cit.*, pp. 660–818; H. S. Washington, *The Chemical Analysis of Rocks*, 4th edition, New York, 1930.

## TABLE X.

| Large Quantities of— | From Small Quantities of— | | | | | |
|---|---|---|---|---|---|---|
| | Arsenic. | Antimony. | Tin. | Lead. | Copper. | Bismuth. |
| A. Arsenic . | ... | 1 (6). Ammonium carbonate. | 2 (11). Ammonium carbonate. | 3 (16). Sodium sulphide. | 4 (21). Sodium sulphide. | 5 (26). Sodium sulphide. |
| Antimony . | 6 (1). $H_2S$ in strong HCl. | ... | 7 (12). $H_2S$ in 15 per cent. HCl. | 8 (17). Potassium sulphide. | 9 (22). Potassium sulphide. | 10 (27). Potassium sulphide. |
| Tin . . | 11 (2). $H_2S$ in strong HCl. | 12 (7). Metallic iron. | ... | 13 (18). Sodium sulphide. | 14 (23). Sodium sulphide. | 15 (28). Sodium sulphide. |
| Lead . . | 16 (3). $H_2SO_4$. | 17 (8). $H_2SO_4$ and tartaric acid. | 18 (13). Nitric acid. | ... | 19 (24). $H_2SO_4$. | 20 (29). As BiOCl. |
| Copper . | 21 (4). By ferric chloride and ammonia. | 22 (9). Same as 21; or thiocyanate and tartaric acid. | 23 (14). Nitric acid. | 24 (19). $H_2SO_4$; or electrolysis. | ... | 25 (30). $H_2S$ and potassium cyanide. |
| Bismuth . | 26 (5). $H_2S$ in strong HCl. | 27 (10). $HNO_3$ (collector: stannic acid). | 28 (15). Metallic iron. | 29 (20). As $PbSO_4$ in 1 : 5 $H_2SO_4$; or metallic iron. | 30 (25). As $BiO.NO_3$. | ... |
| | Iron. | Aluminium. | Manganese. | Zinc. | Nickel. | Calcium. |
| B. Iron . . | ... | 31 (36). As phosphate; or by ether. | 32 (41). Zinc oxide; or by ether. | 33 (46). $H_2S$ in formic acid; or by ether. | 34 (51). Zinc oxide; barium carbonate; or by ether. | 35 (56). As calcium oxalate in oxalic acid. |
| Aluminium . | 36 (31). FeS in tartrate solution. | ... | 37 (42). NaOH $+Br_2$. | 38 (47). $H_2S$ in acetic acid. | 39 (52). NaOH $+Br_2$. | 40 (57). Same as 35. |
| Manganese . | 41 (32). Zinc oxide; or basic acetate. | 42 (37). Zinc oxide; or hexamine. | ... | 43 (48). $H_2S$ in acetic acid. | 44 (53). Dimethylglyoxime. | 45 (58). $H_2SO_4$ and alcohol. |
| Zinc . . | 46 (33). Ammonia. | 47 (38). Ammonia. | 48 (43). Bromine. | ... | 49 (54). NaOH $+Br_2$. | 50 (59). Oxalate. |
| Nickel . | 51 (34). Ammonia. | 52 (39). Ammonia. | 53 (44). Bromine. | 54 (49). $H_2S$ in faintly acid solution. | ... | 55 (60). Oxalate. |
| Calcium . | 56 (35). Ammonia. | 57 (40). Ammonia. | 58 (45). Bromine. | 59 (50). Ammonium sulphide. | 60 (55). Ammonium sulphide. | ... |

the amount of which may vary with the size of grain and degree of weathering of the mineral, the nature and quantity of acids used, the time of contact, and the temperature of decomposition. Thus the insoluble is generally higher with sulphuric than with hydrochloric acid. Even when working under the same conditions the results of duplicate trials may sometimes disagree; of this the following is an example (from H. Ries, *Clays*, 1908, p. 69):

| Successive Treatment with HCl and $H_2SO_4$. | Muscovite. | | Biotite. | |
|---|---|---|---|---|
| 1. Soluble in hydrochloric acid . . | 18·64 | 17·80 | 77·73 | 73·34 |
| 2. Soluble in sulphuric acid . . | 38·75 | 41·80 | 2·04 | 7·88 |

Another source of error lies in the fact that silicic acid resulting from decomposition of silicates is not quite insoluble even after careful dehydration, a few milligrams being always recovered from the filtrate upon evaporation to dryness; even then a small fraction still remains soluble, and part of this is precipitated along with alumina in the subsequent treatment.

Generally speaking, hydrochloric is to be preferred to sulphuric acid in the separation of the insoluble. Bartyes is soluble in hot concentrated sulphuric acid, and reprecipitated on dilution; the precipitate almost invariably carries down other sulphates, especially lead, which it tenaciously retains. A substantial amount of fluorite in the gangue will cause loss in silica if the usual acid treatment is applied, while glass or porcelain may be slightly attacked and yield soluble bases. The method of Berzelius is available for the determination of fluorine and silica in ores containing them (Procedures 13 and 14).

Unless the gangue is composed entirely of altogether insoluble material, such as quartz or barytes, the insoluble figure gives no exact indication of the amount of gangue; the weight is simply that of the unattacked portion, *plus* any silica that may have separated. The distinction between, and separation into, a soluble and insoluble fraction is thus more or less arbitrary and imperfect, and based merely upon the action of the common acids on minerals. In order to obviate the errors to which the separation of the insoluble is liable, the following points should be kept in mind:

(*a*) The decomposition is done, wherever possible, with hydrochloric acid, with or without a nitric-acid treatment; the assay is evaporated to complete dryness, preferably on a water-bath.

(*b*) The filtrate from the insoluble is again evaporated to complete dryness to recover soluble silica.

(*c*) The portion in which the insoluble is determined must also serve for the estimation of all the earths and silicate-forming bases, because silicates are not always attacked to the same extent.

(*d*) It must not be forgotten that hydrous silicates may be present, which lose their water on ignition. Weighing the residue on a tared filter previous to ignition would not give the whole of the combined water, as some may have been lost through the partial decomposition of silicates in the acid treatment. (For estimation of combined water see § VII.)

(*e*) Many mineral products contain organic or carbonaceous (graphitic) matter, which remains with the insoluble residue. In case hydrous silicates are present, the usual method of weighing the insoluble before and after ignition would produce erroneous results; it is therefore best to treat the insoluble from another portion with hydrochloric and hydrofluoric acids to break up the silicates, and to collect on a tared filter after evaporating and taking up with dilute acid. After weighing, the filter is incinerated and the ash subtracted.

§ **V. Determination of Heavy Metals.**—In order to minimize chances of error in the analysis of ores the decomposition of which is tedious or difficult, the heavy metals present should be determined in the same portion as the bases and insoluble residue. On the other hand, while the behaviour of silicates to acids may be uncertain, the decomposition of sulphides is in most cases a simple matter; therefore, where several heavy sulphide metals are present, the separation of which would entail much care and manipulation, it is legitimate, for the sake of expediency in technical work, to estimate some of them along with the lighter metals, and the remainder in a separate portion. A few examples may here be given:

(*a*) If copper, antimony, and tin are present in the hydrogen sulphide precipitate, it is convenient to determine the tin in the first portion after precipitating copper and antimony by means of metallic iron; while in the other portion copper is separated by treating the sulphides with potassium sulphide, tin not interfering in the volumetric determination of antimony by permanganate.

(*b*) If the filtrate from iron and alumina contains zinc, lime, and magnesia, the two latter are precipitated as usual, zinc not interfering; in another portion, the same filtrate is used for the volumetric assay of zinc.

(*c*) With ores containing lead, antimony, or arsenic as principal or important constituents, the decomposition by strong sulphuric acid alone presents advantages as regards separation and estimation of these metals. Lead is converted into sulphate, which is filtered off and dissolved in ammonium acetate. The solution is filtered from the gangue, reprecipitated with sulphuric acid, and concentrated by evaporation. The original sulphate precipitate is apt to include small quantities of antimony, bismuth, iron, or lime, which remain dissolved in the liquor on reprecipitating the lead. Arsenic and antimony are converted into their lower oxides, or, if present in the quinquevalent state, are reduced by filter-paper added to the strong acid, and boiling till colourless. Tervalent arsenic, unlike quinquevalent, is readily precipitated by hydrogen sulphide, and at the same time is separated from antimony after the addition of twice the volume of strong hydrochloric acid to the filtrate from the lead sulphate. The filtrate from the arsenic precipitate is partially neutralized for the precipitation of antimony sulphide, to which is added the small quantity recovered from the filtrate of the reprecipitated lead sulphate.

§ **VI. Separate Determination of Certain Constituents.**—In addition to the general method outlined in §§ IV and V, separate portions must be taken for elements present in minute quantity, or for operations necessitating the use of special apparatus and reagents undesirable in the combination scheme.

*Elements Present in Small Quantities.*—The most important and common example is the gold and silver assay, which is done by crucible fusion or scorification. Any element occurring in small quantity may at times have to be tested for separately on a larger quantity of ore, especially where it constitutes an objectionable impurity. Of this the determination of cadmium in zinc blende is a typical example: the fact that it always occurs in small proportion, and that its precipitation by hydrogen sulphide is a delicate operation, renders a separate estimation desirable, especially as the result is of great importance to the smelter.

The other assays of this class include:

(*a*) *Sulphur.*—Whether the assay involves a fusion or not, sulphur is always estimated separately. It should not be determined in solutions having undergone treatment with hydrogen sulphide, as small quantities of sulphuric acid may be formed in the presence of oxidizing compounds.

(*b*) *Fusion assays*, such as:

Potassium cyanide for tin (in presence of tungsten).
Sodium hydroxide or peroxide, for tin or antimony.
Sodium carbonate and potassium nitrate, for arsenic or antimony.
Sodium carbonate and sulphur, for arsenic or antimony.
Calcium carbonate and ammonium chloride, for alkalis.

(*c*) *Distillation assays*, for mercury, arsenic, fluorine, boric acid.

(*d*) *Gasometric methods.*—Nitric acid, carbon dioxide.

(*e*) *Decompositions* by means of hydrofluoric acid.

(*f*) *Determinations* involving the use of organic acids.

§ **VII. Oxide Minerals.**—Besides the operations so far described, the analysis of minerals other than sulphides may require the determination of combined water, carbon dioxide, or of oxygen present in various forms of combination. Thus oxides, peroxides, hydroxides, carbonates, sulphates, or hydrous silicates may be present. The analysis is carried out as follows:

1. *Silica and total metals* are determined in one portion, or two if more convenient.

2. *Total combined water* (in hydroxides, hydrous sulphates, and silicates, etc.): direct estimation by Penfield's method.[1]

3. *Carbon Dioxide.*—This is most conveniently estimated in a Geissler or similar apparatus by decomposition with an acid.[2] For clean carbonates, fusion with borax answers well.[3]

4. *Sulphuric Anhydride.*—Sulphates of barium and strontium require fusion with sodium carbonate; those of lead and lime are opened up by boiling with ammonium carbonate; basic sulphates dissolve in dilute acids. The determination differs from that of sulphur in that no oxidizing agent is used.

5. *Differentiation between Higher and Lower Oxides.*—The following commoner elements occur in ores in different states of oxidation: iron, manganese, cobalt, chromium, antimony, and arsenic. Therefore, if found to be present, it will be necessary to ascertain their state of oxidation.

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[1] *Amer. J. Sci.* (3), 1894, **48**, 30.

[2] Direct determination, Hillebrand and Lundell, *op. cit.*, p. 623.

[3] Fresenius, *Quantitative Chemical Analysis*, 7th edition, 1876, p. 336.

*Iron.*—Ferrous oxide is usually determined by decomposing the ore in an atmosphere of carbon dioxide and titrating with permanganate, ferric oxide being found by difference. Chalybite and vivianite are soluble in dilute sulphuric acid; magnetite and ilmenite are opened up by fusion with bisulphate, silicates by hydrofluoric acid.[1] Very often the direct determination of ferric iron is more convenient, since ferric compounds are more readily dissolved than ferrous (*e.g.* in silicates, spinels, etc.). The ore is attacked with hydrochloric acid in an atmosphere of carbon dioxide, and the hot solution titrated with stannous chloride till colourless. Copper or arsenates must not be present.

*Manganese.*—The intermediate oxides act like mixtures of the monoxide and the dioxide, which latter is determined by oxalic acid, or ferrous ammonium sulphate, and permanganate. The higher oxides of manganese interfere with the determination of ferrous oxide, and *vice versa*; they react upon one another with formation of ferric and manganous salts, though the amount of excess oxygen can, of course, be correctly ascertained.

*Cobalt.*—A higher oxide occurs in the mineral asbolan. It can be determined in the same manner as manganese dioxide, as well as by distillation with hydrochloric acid and potassium iodide.

*Chromium.*—Chromic oxide is found in some bauxites; combined with ferrous oxide it occurs as chromite, which always contains more or less ferric iron. The ferrous oxide is determined by heating 0·5 g. of the finely powdered mineral with 10 ml. of sulphuric acid (sp. gr. 1·34) in a pressure tube at 250° to 300° C. for ten hours (paraffin bath) and titrating the solution with permanganate. Chromates are determined similarly to manganese dioxide, by solution of the mineral in an acid solution of ferrous sulphate, and titration of the excess of ferrous salt.

*Antimony.*—Oxide ores may contain tri- and tetroxide, the former being soluble in tartaric or dilute hydrochloric acid. Total antimony is determined by fusion with sodium carbonate and sulphur, and the insoluble oxide found by difference.

*Arsenic.*—To differentiate between arsenious and arsenic acid the mineral is boiled with caustic alkali. The arsenite in the filtrate may be titrated with iodine, or the arsenate with iodide and thiosulphate.

§ **VIII. Mixed Oxide and Sulphide Ores.**—If the sample under examination contains both oxide minerals and sulphides, the latter will interfere with the determination of combined water and carbonic acid described under § VII. It also becomes necessary to estimate the metals present as oxides.

1. *Combined Water.*—Direct estimation in a Penfield tube by adding ignited litharge or bismuth oxide as a retainer for sulphur. In presence of fluorides, ignited lime is mixed with the substance.

2. *Carbon Dioxide.*—The ore is decomposed by a mineral (but not hydrochloric) acid, and sufficient potassium chromate to oxidize the sulphides, or an organic acid, such as tartaric acid, may be used. Calcite is decomposed by bichromate solution alone, without the addition of an acid.

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[1] Hillebrand and Lundell, *op. cit.*, p. 781.

3. *Sulphur as Sulphides and Sulphates.*—Minerals containing sulphur may be classified as follows according to their solubilities:

(*a*) Sulphates soluble in water ("vitriols").

(*b*) Sulphates of calcium and lead, and basic sulphates (*e.g.* brochantite), soluble in hydrochloric acid, or decomposed by boiling ammonium carbonate solution.

(*c*) Sulphides soluble in hydrochloric acid (*e.g.* galena, blende, stibnite).

(*d*) Sulphides insoluble in hydrochloric acid (*e.g.* pyrites, sulphides of copper).

(*e*) Insoluble sulphates (of barium and strontium).

Extraction with ammonium carbonate solution yields a solution of sulphur trioxide from (*a*) and (*b*); nitric acid and potassium chlorate dissolve the sulphur from (*c*) and (*d*); the sulphuric anhydride in the insoluble residue from this treatment is determined after fusion with sodium carbonate.

Barium (or strontium) carbonate, which forms an occasional gangue mineral of sulphide ores, interferes with the determination of sulphide sulphur by being converted into insoluble sulphate. In such a case the alkaline earth carbonate is removed by a preliminary treatment with acetic acid.

4. *Differentiation between Oxides, Sulphides, etc.*—In estimating oxides of metals in presence of their sulphides, advantage is taken of the different behaviour of minerals towards certain reagents, which dissolve some while leaving others unaffected. The same principle is applied in separating various oxidized minerals from one another.

The percentage of total metals, sulphur, silica, etc. having been determined as described in the preceding subsections, a fresh portion of sample is attacked with a suitable solvent and the resulting solution examined for metals by the usual methods, while the residue is subjected to extraction by another solvent if necessary.

A scheme for the separation of the more important minerals of the common metals is outlined in Table XI, in which the vertical columns indicate the order in which the reagents are used; these are distinguished by lettering (A, B). The horizontal lines show the order of solution of the minerals. Some are soluble in reagents placed in successive vertical columns; this is indicated by arrows inserted between the names.

The procedure outlined in the table separates the ore into an "insoluble residue" and "soluble fraction," much in the same manner as does hydrochloric acid or *aqua regia* in the determination, described in § IV, of the insoluble gangue and total metals; but what has been said there with regard to the behaviour of silicates towards acids applies to a much greater extent to the separation of minerals by selective decomposition. Not only does the degree of decomposition vary with the temperature, quantity, and concentration of solvent used, the time of contact, and the degree of comminution, but the dissolved constituents themselves may exert a slight solvent action. Moreover, crystalline varieties are often less soluble than amorphous ones. The solubility may also be affected by impurities or isomorphous replacements. In this manner a small amount may escape solution, or be dissolved, by a reagent contrary to the ordinary behaviour

## TABLE XI.

| | 1.<br>Water. | 2.<br>A. Acetic, or<br>B. Tartaric Acid. | 3.<br>A. Caustic Soda, or<br>B. Ammonia. | 4.<br>Hydrochloric Acid:<br>A. Dilute.<br>B. Strong. | 5.<br>Nitric Acid. | 6.<br>Fusion with Sodium—<br>A. Bisulphate, or<br>B. Carbonate. | 7.<br>Fusion with Sodium—<br>A. Hydroxide, or<br>B. Peroxide. |
|---|---|---|---|---|---|---|---|
| **Lead** | ... | A. Carbonate. | A. Sulphate. | A, B. Sulphide. → | Sulphide. | ... | ... |
| **Copper** | Sulphate. | A. Carbonates, Oxides, Basic sulphates, Oxychloride. | → B. | B. Silicates. | Sulphides, Arsenides, Antimonides. Native. | ... | ... |
| **Silver** | ... | ... | B. Chloride. | ... | Sulphide, Arsenides, etc. Native. | ... | ... |
| **Antimony** | ... | B. Trioxide. → | A. Trioxide, Sulphide. → | A, B. Sulphide. → | Sulphide.[1] | ... | A. Tetroxide. |
| **Tin** | ... | ... | ... | ... | Sulphide.[2] | ... | B. Oxide. |
| **Iron** | Sulphate. | A, B. Carbonate. | ... | B. Oxides.[3]<br>A, B. Hydroxides, Pyrrhotite. → | ...<br>Pyrites, Arsenides, Pyrrhotite. | A. Ilmenite, Magnetite, Chromite. →<br>B. Silicates. | B. Chromite. |
| **Zinc** | Sulphate. | A. Carbonate (in 50 per cent. acid). → | A. Carbonate, Silicate. | A, B. Sulphide. → | Sulphide. | A, B. Zinc spinels.[4] | ... |
| **Nickel (cobalt)** | Sulphates. | Carbonates. | ... | Arsenates.<br>B. Ni silicate. | Sulphides. Arsenides. | A, B. Ni silicate. | ... |
| **Manganese** | ... | Carbonate. | ... | Sulphide,[5]<br>Dioxides. | Sulphide. | B. Silicates. | ... |
| **Calcium** | Sulphate.[6] | Carbonate. | ... | A. Phosphate. | ... | B. Silicates. | ... |
| **Barium** | ... | Carbonate. | ... | ... | ... | B. Sulphate. | ... |

[1] Separation of sulphide from tetroxide by hydrochloric or nitro-tartaric acid.
[2] Stannine: dissolve in *aqua regia*.
[3] Some oxide ores are difficultly soluble in hydrochloric acid: fuse with bisulphate.
[4] Addition of borax glass advisable when sodium carbonate is used.
[5] In zinc blende.
[6] If much sulphate is present, extract with sodium sulphate or chloride solution.

of the mineral. If thereby metals present as sulphides are calculated to oxides, or *vice versa*, the final summation will be affected. It should therefore be borne in mind that separations by fractional decomposition, while quantitative in many cases, are far from satisfactory in others. At times it is practically impossible to establish the exact composition of a complex ore by direct analysis, in which case it is legitimate to compute the quantity of one or more oxides present by calculation on the assay results. The mineralogical examination is the most valuable help where chemical methods fail.

Where hydrochloric acid dissolves both the sulphides and oxides of the same metal, the order of the reagents in columns 4 and 5 of the table may be inverted, thus:

| | 4. | 5. | 6. |
|---|---|---|---|
| | Nitric Acid. | Hydrochloric Acid. | A. Sodium Bisulphate.<br>B. Sodium Carbonate. |
| Iron . . | Pyrites, arsenides, pyrrhotite. | Hydroxides, oxides. | A. Oxides. |
| Manganese . | Sulphide. | Dioxides. | B. Silicates. |

Pyrrhotite may also be separated from pyrites, limonite, etc. by means of a horseshoe magnet.[1]

§ **IX. Determinations by Difference.**—When constituents are determined by difference, the following rule is observed wherever possible: After the sum of the constituents has been ascertained, the subordinate is estimated direct and the predominant found by difference. If the reverse is done, though this may not affect the final result, the experimental error is all thrown on the side of the subordinate element, and the smaller its amount the less reliable will be the figure so obtained. To take one constituent by difference, by subtracting the sum of all the others from 100·00, is an objectionable practice in mineral analysis; it is admissible only in the case of refined metals, the fineness of which is ascertained by determining the impurities.

The "loss on ignition method" for the estimation of combined water can be used only occasionally, as with some oxide minerals, such as bauxite, limonite, and certain silicates. Organic matter, carbonates, sulphides, sulpharsenides, etc. cause high results, while ferrous compounds lower them. With a little practice, Penfield's direct determination of combined water is almost as simple as that by loss on ignition.

In a few cases carbon dioxide and combined water can be estimated together by loss on ignition—*viz.* with oxide ores free from sulphur, consisting of carbonates of copper, zinc, or lead, with or without ferric oxides or hydroxides. This is done at a gentle heat in a porcelain crucible, care being taken to avoid reduction of its contents by the burner gases.

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[1] Lunge, Keane, and Thorne, *Technical Methods of Chemical Analysis*, 2nd edition, London, 1924, **1**, 383.

§ **X. Accuracy : " Traces."**—Concerning the degree of accuracy to be attained, a final error of ±0·50 per cent. should not be greatly exceeded, and a complete analysis which sums up to between 99·50 and 100·50 is very satisfactory. The results are calculated to the second decimal place. To go beyond this is useless in practical ore analysis.

The use of the term " trace " may here be considered, as opinions differ regarding the amount to which it should be applied. However, from the point of view of technical ore analysis, we may define as " trace " a quantity that does not affect the final result, *i.e.* less than 0·01 per cent. (This does not, of course, apply to noble metals, which are calculated to ounces per ton.)

In scientific work (*e.g.* geochemistry, genesis of ore deposits, distribution of elements, etc.) a full analysis also includes the determination of elements present in " spectroscopic " traces, and often involves the working up of large quantities of material. The description of such work is beyond the scope of this book, and it must be understood that the term " complete analysis " is applied throughout to the estimation of the technically important constituents of mineral substances, consumed and produced in the metallurgical and chemical industries, by the analytical methods described in this manual.

## V.—LITHIUM.

§ **I. Minerals.**—(*a*) *Amblygonite* (*montebrasite*), lithium aluminium fluophosphate, $Li(AlF)PO_4$. White, yellow, green, or brown triclinic crystals easily cleavable. Soluble in sulphuric acid. H. 6; sp. gr. 3·01–3·09. The most important source of lithium.

(*b*) *Spodumene*, $LiAl(SiO_3)_2$, belongs to the monoclinic pyroxene group. Greenish or greyish, translucent crystals of pearly lustre. H. 6·5–7; sp. gr. 3·13–3·20.

(*c*) *Polylithionite*, a greenish mica, $KLi_2AlSi_4O_{10}F_2$. H. 2·5–4; sp. gr. 2·8–3·3. Generally contains some rubidium. High in fluorine and low in water.

(*d*) *Lepidolite*, composition variable, ranging from that of polylithionite to that of lithium-bearing muscovite, for example, $K_4Li_7Al_5.Al_2Si_{14}O_{40}(F,OH)_8$. H. 2·5–4; sp. gr. 2·8–3·3. Purple, lilac, pale blue, or nearly white. Also carries some rubidium, but less fluorine and more water than polylithionite. *Zinnwaldite* is an iron-lithium mica.

(*e*) *Taeniolite*, $KLiMg_2Si_4O_{10}F_2$, a mica intermediate in composition between muscovite and talc in which the group $LiMg_2$ occurs in place of $Al_2$ and $Mg_3$ respectively. White with a silky lustre. Sp. gr. 2·82.

(*f*) *Petalite*, $LiAl(Si_2O_5)_2$, is usually massive. Colourless or white, transparent to translucent. H. 6–6·5; sp. gr. 2·39–2·46. Practically unattacked by acids.

(*g*) *Triphylite* and *lithiophylite* are lithium iron manganese phosphates, $Li(Fe,Mn)PO_4$. Orthorhombic, lustre vitreous to resinous. H. 4·5–5·5; sp. gr. 3·42–3·56. The colour of the former, in which iron predominates, is greenish-grey to bluish; the latter, containing more manganese, is salmon-coloured to yellowish-brown.

(*h*) *Beryl* (*q.v.*, **VII,** § I, *a*, 4) may contain some lithia.

(*i*) Lithium is widely distributed in small quantities in many alkali minerals, *e.g.* felspars, micas, and rocks containing them. Through the disintegration of the latter the lithium is converted into soluble salts, hence it occurs in spring and mineral waters and in soils. It is absorbed by vegetable organisms and has been detected in many plant ashes.

§ **II. Properties and Compounds.**—(*a*) The *metal* is obtained, as is sodium, by electrolysis of fused salts. It is silver-white on fresh surfaces, softer than lead, and the lightest solid (sp. gr. 0·54). Its melting-point is 180° C.; it combines directly with oxygen to $Li_2O$, hydrogen to LiH, nitrogen to $Li_3N$, and with the halogens. Acids dissolve it with ease, and water is decomposed by it, though not violently.

(*b*) *Lithium hydroxide*, LiOH, is formed by the action of the metal on water, or by double decomposition between lithium sulphate and barium hydroxide. Colourless crystals, $LiOH.H_2O$, which lose their water of hydration when heated in a current of hydrogen.

(*c*) *Lithium chloride*, LiCl, obtained by solution of the hydroxide or carbonate in hydrochloric acid, forms colourless, extremely deliquescent crystals, very soluble in water, also in many alcohols and in pyridine. The salt melts at 606° C. Evaporation of its aqueous solution to dryness causes very slight hydrolysis; the residue is not quite completely soluble in pyridine, and imparts an alkaline reaction to water.

(*d*) *Lithium chloroplatinate*, $Li_2PtCl_6.6H_2O$, resembles the sodium salt and is readily soluble in water and in alcohol.

(*e*) The *nitrate*, $LiNO_3$, is isomorphous with sodium nitrate; very soluble in water and in alcohol.

(*f*) *Lithium sulphate*, $Li_2SO_4.H_2O$; soluble in water and in alcohol.

(*g*) *Lithium carbonate*, $Li_2CO_3$, is a white crystalline powder, obtained when a concentrated solution of the chloride is poured into an ammoniacal solution of ammonium carbonate and the liquid is heated. 100 parts of water dissolve 1·4 parts at 10° C., and 0·73 part at 100° C. It is more soluble in the presence of salts of sodium and potassium, and much more so in the presence of ammonium salts. The carbonate is completely dissociated when heated to 780° C. in a current of hydrogen.

(*h*) *Trilithium phosphate*, $2Li_3PO_4.H_2O$, is precipitated by addition of sodium phosphate solution to solutions of lithium salts. The precipitation is not complete unless caustic soda is added to neutralize the free acid formed: $3Li_2SO_4 + 2Na_2HPO_4 = 2Li_3PO_4 + 2Na_2SO_4 + H_2SO_4$. The crystalline precipitate becomes anhydrous at 100° C. It is soluble in 2539 parts of water or 3920 parts of dilute ammonia, but is much more soluble in the presence of ammonium salts.

(*i*) The *fluoride*, LiF, is precipitated from lithium solutions by ammonium fluoride. It is soluble in 800 parts of water.

§ **III. Quantitative Separation.**—(*a*) Lithium, like the common alkalis sodium and potassium, remains in solution after precipitation of metals of the other analytical groups. For the separation of alumina the basic acetate process should be adopted, as the hydroxide precipitated by ammonia retains lithium. The separation of the alkaline-earth group with ammonium carbonate must be carried out in the presence of considerable ammonium chloride, and the precipitate thoroughly washed with hot water (*cf.* § II, *g*); it is advisable to dissolve the precipitate in hydrochloric acid and repeat the precipitation. Calcium oxalate precipitated in presence of lithium is always contaminated with the latter, and it is difficult to effect complete removal by washing. Magnesium is precipitated by barium hydroxide and the excess of barium removed by ammonium carbonate. At this point sulphates, borates, and other salts must be converted into chlorides. The solution is then evaporated and the residue gently ignited for the removal of ammonium salts.

In the analysis of minerals, the first step in the determination of lithium usually consists in the application of J. Lawrence Smith's method (ignition with calcium carbonate and ammonium chloride), which yields the mixed alkali chlorides free from other salts.

(*b*) *Separation from the Other Alkali Metals.*—This is based on the solubility of lithium chloride in certain organic solvents, in which the chlorides of the other alkali metals are practically insoluble.

(1) *Ether-alcohol method.* The mixed chlorides are dissolved in a very little water and transferred to a small flask (a 30-ml. glass-stoppered conical flask is large enough for most analyses). The solution is evaporated to dryness on the steam-bath. To the salts are added 0·4 ml. of water (usually sufficient with warming) and 0·02 ml. of concentrated hydrochloric acid (a third of a drop). Then 5 ml. of absolute alcohol is added slowly, the flask is rotated, and 15 ml. of absolute ether added. After about 15 minutes the solution is filtered through a small wad of asbestos supported by glass-wool in a suction filter. The lithium chloride in the filtrate is converted into sulphate by heating with a slight excess of sulphuric acid. The sulphate is ignited and weighed. Only cæsium is likely to contaminate the lithium sulphate; it may be detected and separated from the lithium as cæsium chloroplatinate, insoluble in alcohol, and the weight of the lithium corrected accordingly. However, this correction is unnecessary if potassium, rubidium, and cæsium have been previously separated from sodium and lithium as chloroplatinates.

(2) *Amyl alcohol method.*[1] The concentrated solution, containing less than 0·2 g. of the mixed chlorides and a few drops of hydrochloric acid, is treated in a small conical flask with 10 ml. of amyl alcohol (b.p. 129°–132° C.), and cautiously heated on an asbestos gauze; the flask is provided with a capillary tube, passing through a doubly perforated stopper and dipping into the liquid, through which air is passed by aspiration to facilitate boiling. When all the water and part of the alcohol have been driven off, the liquid is allowed to cool; 2 to 3 drops of strong hydrochloric acid are then added to convert into chloride the small quantity of lithium hydroxide formed by hydrolysis. The liquor is boiled for a short time, and filtered whilst hot through asbestos. The residue is carefully washed with boiled amyl alcohol, the filtrate and washings evaporated to dryness in an air-bath,

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[1] F. A. Gooch, *Amer. Chem. J.*, 1887, **9**, 33.

the residue dissolved in dilute sulphuric acid, and filtered from organic residue into a tared platinum crucible; this solution is evaporated to dryness, the residue gently heated till fused, the crucible covered, cooled, and weighed. If the proportion of lithium in the mixed chlorides is small, the residue from the extraction with amyl alcohol should be dissolved in water and the treatment repeated. As the weighed lithium sulphate contains small quantities of the other alkalis, a correction must be applied. For every 10 ml. of alcoholic filtrate (exclusive of the alcohol used for washing) the following deduction is made from the weight found:

0·0005 g. if sodium is present;
0·00059 g. if potassium is present;
0·00109 g. if both sodium and potassium are present.

The solubility of rubidium and cæsium chlorides is of the same order (*i.e.* 0·0009 g. per 10 ml.). If sodium and potassium are also determined, corresponding additions must be made to the weight of the chlorides, *i.e.* 0·00041 g. for sodium and 0·00051 g. for potassium per 10 ml. of alcoholic liquor.

(*c*) *Separation from Large Quantities of Sodium and Potassium.*—The solution of the chlorides is concentrated as much as possible, and saturated with hydrochloric acid gas introduced into the flask by means of a tube, the enlarged end of which terminates just above the level of the liquid. Most of the sodium and potassium are precipitated as chlorides. The acid liquor is filtered through asbestos, and the precipitate thoroughly washed with strong hydrochloric acid. The filtrate and washings, containing all the lithium and a little potassium and sodium, are evaporated to dryness, the residue is dissolved in water, a few drops of hydrochloric acid are added, and the solution is treated as under (*b*).

§ **IV. Gravimetric Determination.**—Lithium is determined gravimetrically as the sulphate; this is the most convenient method, and the precautions required in the determination of sodium and potassium as sulphates are unnecessary, as no acid lithium sulphate is formed. The determination of lithium as sulphate has been described under § III, *b*.

The purity of the weighed lithium sulphate may be checked, if desired, by solution in 0·01N. hydrochloric acid and precipitation of the sulphate ion with barium chloride.[1] The boiling solution (about 350 ml.) is stirred and precipitated drop by drop with 5 per cent. barium chloride (twice the amount necessary for complete precipitation), kept near the boiling-point for ten minutes, set aside overnight, and decanted through a filter. The precipitate is digested on the water-bath for two hours with about 300 ml. of distilled water, which is stirred from time to time, and then allowed to cool. The precipitate is collected with a minimum of hot water, dried, separated from the paper, ignited, and weighed.[2]

§ **V. Volumetric Determination.**—Lithium hydroxide or carbonate may be determined by the ordinary processes of alkalimetry. 1 ml. of

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[1] J. N. Friend and W. N. Wheat, *Analyst*, 1932, **57**, 559.

[2] $Li_2SO_4 \times 2{\cdot}124 = BaSO_4$.

0·1N. acid ≡ 0·001494 g. of $Li_2O$. Lithium chloride may be titrated argentometrically.

§ VI. **Detection in Minerals.**—(*a*) Lithium compounds and minerals impart to the flame a beautiful crimson colour. The test is more sensitive if the material is first moistened with concentrated hydrochloric acid; some minerals require fusion with potassium bisulphate and acid fluoride in a loop of platinum wire. The colour is masked by the yellow sodium flame, but can be distinguished through a screen of blue glass or by means of the spectroscope. The spectrum of lithium has a bright red line, 6708A., about midway between the red potassium line and the sodium line. If this line is intense and persistent the mineral probably contains a weighable quantity of lithium. The limit of visibility varies somewhat with conditions and with different observers, but as little as $10^{-6}$ mg. of lithium can be detected. A small coil of platinum wire dipped into a solution containing about $2 \times 10^{-5}$ mg. per ml. and held in a Bunsen flame will produce a transient appearance of the red line. A method for the estimation of these small quantities of lithium, such as are found in mineral waters,[1] for example, consists in measuring the dilution of the unknown solution at which the line is barely detectable, and comparing it with the dilution of a similar known solution. The gravimetric method is so simple, however, that for moderate and relatively large quantities of lithium it is much to be preferred to the spectroscopic process.

(*b*) If it is desired to prove the presence of lithium by a wet reaction, the finely powdered mineral, if a silicate, is opened up with hydrochloric and hydrofluoric acids; the fluorides are decomposed by evaporation with hydrochloric acid, and the chloride solution is diluted and precipitated with baryta water. Phosphate minerals are best treated by J. L. Smith's method, and the ignited products leached with hot water. After either treatment the alkaline earths are precipitated in the filtrate with ammonium carbonate, the solution is filtered and evaporated to dryness, and the ammonium salts are expelled by gentle ignition. The residue is extracted with alcohol-ether and a drop of hydrochloric acid, and the filtered extract evaporated to dryness. The residue is dissolved in a very little water and the solution divided into two parts. One is treated with sodium phosphate and a slight excess of caustic soda. The residue left after evaporation to dryness is taken up with a minimum of warm water followed by an equal volume of ammonia. The phosphate precipitate is soluble in hydrochloric acid and the solution remains clear on the addition of ammonia; but on boiling a heavy crystalline precipitate is produced. The other half of the solution is heated with its own volume of a 2N. solution of sodium carbonate (§ II, *g*); the washed carbonate precipitate may be converted into chloride and the latter tested in the spectroscope. The lithium carbonate precipitate is not formed, however, unless the quantity of lithium exceeds 3 mg. per ml.

§ VII. **Determination in Minerals.**—The procedure for the determination of lithium in minerals and rocks does not differ from that followed for sodium and potassium up to the point where the pure mixed alkali chlorides are obtained. If much lithium is thought to be present, it is better to separate it at once before attempting to weigh the chlorides of sodium, etc. on account of the hygroscopicity of lithium chloride. Of the different methods available for extracting the alkalis that of J. Lawrence Smith is most satisfactory, though decomposition with hydrofluoric acid, or fusion with lead oxide or bismuth oxide, may also be adopted. However obtained, the alkali chlorides are transferred to a small conical flask, and the determination of lithium is concluded as explained in § III, *b*.

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[1] Skinner and Collins, *U.S. Dept. of Agriculture, Bureau of Chemistry Bull.*, 1912, p. 153.

§ **VIII. Complete Analysis of Minerals.**—In complete analyses involving alkali metals, the determination of the latter is nearly always carried out on a separate portion of mineral, which is usually treated by J. Lawrence Smith's method. Silica, alumina, and common bases are determined in another portion by fusion with sodium carbonate, etc. as usual.

Amblygonite is analysed as under **IV,** Procedure 13, the alkalis being determined in another portion as explained *above*; soda replaces lithia to a considerable extent in certain varieties.

The most interesting silicate mineral is lepidolite, which in addition to lithia may contain as much as 3 per cent. of rubidia, as well as cæsia (0·7 per cent.). (See **VI,** § III, *d*.)

## VI.—RUBIDIUM AND CÆSIUM.

§ **I. Minerals.**—(*a*) *Rhodizite*, rubidium aluminium borate, $Rb_2O.2Al_2O_3.3B_2O_3$, a very rare mineral, has been found in the form of minute, white, translucent crystals on tourmaline. Tetrahedral; H. 8; sp. gr. 3·4. It contains also cæsium and potassium, but is the nearest approach to a rubidium mineral proper.

(*b*) *Pollucite*, cæsium aluminium silicate, $H_2Cs_4Al_4(SiO_3)_9$, is the only high-grade cæsium mineral known; part of the cæsia is replaced by soda, but rubidia is completely absent. Colourless and transparent; occurs crystallized (cubic) as well as massive. Very rare. H. 6·5; sp. gr. 2·9.

(*c*) *Lepidolite* (*q.v.*, **V,** § I, *d*), though a lithium mineral, is a source of rubidium; some varieties carry as much as 3 per cent. of rubidia, also cæsia (up to 0·7 per cent.).

(*d*) *Vorobyevite* is a variety of beryl containing up to 3 per cent. of cæsia.

(*e*) Rubidium and cæsium are met with in minute quantities in a number of minerals, such as felspars, beryl, micas, leucite, spodumene, carnallite. As much as 3·3 per cent. of rubidia has been reported in microcline. Like lithium, they are dissolved in the process of weathering of silicate rocks, hence traces are found in mineral, spring, river, and sea water, as well as in soils. Rubidia is held more firmly in clays than lithium and potassium, while cæsia is retained more tenaciously than all the other alkalis.

§ **II. Properties and Compounds.**—(*a*) The *elements* may be prepared by reduction of the oxides with calcium, or of the hydroxides by means of aluminium or magnesium. *Rubidium* is very soft and silver-white, but oxidizes very rapidly, and takes fire in air. It burns also when brought into contact with water. Sp. gr. 1·52; m.p. 38·5° C.; b.p. 696° C. Its vapour is blue. *Cæsium*, like rubidium, is silver-white, and takes fire in the air as well as in water. Sp. gr. 1·88; m.p. 26·4° C.; b.p. 670° C.

(*b*) *Hydroxides.—Rubidium hydroxide*, RbOH, is prepared from rubidium sulphate and barium hydroxide by double decomposition; the filtered solution leaves on evaporation a greyish-white deliquescent mass, which is a stronger base than potassium hydroxide. *Cæsium hydroxide*, CsOH, is prepared in a similar manner to the preceding, which it resembles. It is the strongest base known, cæsium being the most electropositive metal.

(*c*) The *chlorides*, *sulphates*, *nitrates*, *carbonates*, and, generally speaking, all rubidium and cæsium salts bear a close resemblance to those of potassium. The carbonates are deliquescent; the cæsium salt is soluble in absolute alcohol. The *alums*, *perchlorates*, *chlorostannates*, and *cobaltinitrites* are more or less difficultly soluble.

(*d*) The *chloroplatinates* are precipitated by chloroplatinic acid as yellow octahedra. The cæsium compound is the least soluble of the alkali chloroplatinates: at 20° C., 100 parts of water dissolve

$K_2PtCl_6$: 1·12 part;
$Rb_2PtCl_6$: 0·14 part;
$Cs_2PtCl_6$: 0·08 part.

(*e*) *Cæsium dichloroiodide*, $CsCl_2I$, is one of the many polyhalides known; recrystallization of this salt has been the means of purifying material used in the determination of the atomic weight of cæsium. Tri- and pentahalides have been prepared.

§ **III. Quantitative Separation.**—(*a*) The separation of rubidium and cæsium from all other metals is effected in a similar manner to that of potassium.

(*b*) *Rubidium from Potassium.*—No exact method for the separation of these closely allied metals is known. Rubidium chloroplatinate is slightly less soluble than the potassium salt, and separation from a small quantity of potassium may be effected in 15 per cent. alcohol. Rubidium chloride is more soluble than potassium chloride, and may be concentrated, like lithium, by treatment of the almost saturated solution with hydrochloric acid or alcohol (**V**, § III, *c*).

(1) If the available quantity of the mixed potassium and rubidium chlorides or sulphates is fairly large and contains a substantial proportion of rubidium salt the two metals can be determined by the indirect method, *viz.* determination of the acid radical.

(2) In the majority of cases the above procedure is not applicable, and the best method is to proceed as under (*d*, 4), *below*.

(*c*) *Cæsium from Rubidium and Potassium.*—(1) If the mixed chlorides are very high in cæsium (as in the case of pollucite) the precipitated chloroplatinates of cæsium, potassium, and rubidium are subjected to several fractional crystallizations, whereby the chloroplatinates of potassium and rubidium are obtained in solution.

(2) If the mixture is low in potassium, the mixed chloroplatinates may be taken up in 15 per cent. alcohol, which will extract about 0·008 g. of

potassium chloroplatinate for each 5 ml. of solution. If more than 5 ml. is used, the rubidium and cæsium begin to dissolve also.

(3) If the mixture is low in cæsium, the method given under (*d*, 2), *below*, effects a rapid concentration; for most cæsium-bearing minerals, double treatment of the chlorides freed from sodium and lithium suffices to obtain all of the cæsium in solution.

(*d*) *Separation of the Five Alkali Metals from One Another.*[1]—It is assumed that the alkalis have been isolated in the form of chlorides, free from other metals (*e.g.* by J. Lawrence Smith's method).

The mixed chlorides are dissolved in a little water and a drop of hydrochloric acid. The solution is treated with an excess of chloroplatinic acid, evaporated to dryness, the residue extracted with 80 per cent. alcohol, the extract filtered, and the insoluble fraction, $R^1$, washed with alcohol.

(1) The alcoholic filtrate is evaporated to dryness with ammonium formate solution, several times if necessary, until colourless. The precipitated platinum is filtered off, washed with water, and the lithium and sodium determined in the filtrate as described in **V**, § III, *b*.

(2) The insoluble residue $R^1$ consists of the chloroplatinates of potassium, rubidium, and cæsium, which are dried and weighed. The operations described *below* aim at the determination of rubidium and cæsium; potassium is determined by difference, being normally present in more or less considerable excess.

The mixed chloroplatinates are transferred to a beaker, the crucible is rinsed with boiling water, and the suspension is evaporated several times with ammonium formate solution until the platinic salt is completely reduced. The precipitated platinum is filtered off and washed, and the filtrate evaporated to dryness in a porcelain dish; the residue is heated very gently until free from ammonium salt, and dissolved in a little water; the solution is transferred to a small conical flask and evaporated to dryness. The residual chlorides are dissolved in 0·4 ml. of hot water; the cold solution is saturated with hydrogen chloride and treated with 10 ml. of alcohol previously saturated with the same gas. The precipitate is collected on a small pad of asbestos in a tiny funnel, and washed with 2 ml. of mixed absolute alcohol and ether. The filtrate is evaporated to dryness in a porcelain crucible, and the dry residue ignited very gently and weighed. If the weight does not exceed 0·0006 g., then rubidium and cæsium are absent; if it does, the precipitate is dissolved in a little water, the solution evaporated as before and the precipitation repeated, the second filtrate being added to the crucible containing the first residue, evaporated to dryness, and the combined residue, $R^2$, gently ignited and weighed.

The double treatment yields two fractions, namely, the residue $R^2$, containing the whole of the cæsium with some rubidium and potassium; and the chloride precipitate, $P^1$, containing the balance of the rubidium and potassium.

(3) *Determination of cæsium.* The following procedure is planned for any quantity of rubidium chloride up to 0·01 g. and any quantity of cæsium chloride up to 0·032 g. The residue $R^2$ is dissolved in a little water; the

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[1] R. C. Wells and R. E. Stevens, *Ind. Eng. Chem.*, *Anal. Ed.*, 1934, **6**, 439.

solution is transferred to a small beaker and evaporated to dryness. The residue is treated with 0·1 ml. of 5 per cent. ammonium sulphate solution, and 5 ml. of a saturated solution of ammonium sulphate in 79 per cent. alcohol[1] is added drop by drop from a burette during constant stirring, a bulky precipitate of potassium and rubidium sulphates beginning to form after addition of a few drops of the precipitant. The precipitate is set aside for half an hour with occasional stirring, collected under slight suction on a small asbestos pad, and washed with three 0·5-ml. portions of alcoholic ammonium sulphate solution containing 0·13 g. of ammonium chloride per 100 ml. (precipitate: $P^2$).

The filtrate containing the cæsium is evaporated to dryness in a small tared platinum crucible on the water-bath, after addition of a little ammonium sulphate. When the salts begin to crystallize a little alcohol is added, and the evaporation is repeated with a few drops of absolute alcohol. The crucible covered with a watch-glass is cautiously heated in a radiator until a slight deposit of ammonium chloride forms on the watch-glass. This is then removed, and the heat carefully increased until all the ammonium salt has volatilized. The residual cæsium sulphate is heated to constant weight exactly as potassium sulphate.

Cæsium may be spectroscopically identified in the weighed sulphate, which is dissolved in 2 to 3 drops of water; a tight coil of platinum wire is dipped into the solution and held in the Bunsen flame. Less than 0·0001 g. of cæsium can thus be detected; the blue lines are considerably nearer the yellow than those of rubidium, the spectroscopic test for which is also much less sensitive.

(4) *Determination of rubidium.* If the amount of cæsium calculated to chloride, *plus* 0·0006 g. of potassium chloride for each treatment with alcoholic hydrochloric acid, accounts for the weight of $R^2$, then rubidium is absent; otherwise it may be distributed between the chloride precipitate $P^1$ and the sulphate precipitate $P^2$. If so, $P^1$ must be treated by the alcohol-hydrogen chloride process described *above* as long as any more rubidium is extracted, an allowance of 0·0006 g. of potassium chloride being made for each extract; the solubility of rubidium chloride under the same conditions is about 0·0027 g. Eight or nine extractions will be sufficient to extract all the rubidium from 0·5 g. of any known mineral except rhodizite, most minerals and rocks not yielding any weighable amount of rubidium.

The combined rubidium fractions, including $P^2$, are dissolved in water, treated with a slight excess of chloroplatinic acid, and evaporated to dryness. The residue is taken up with 15 per cent. alcohol, collected, washed with 95 per cent. alcohol, dried, and weighed as $Rb_2PtCl_6$. The actual presence of rubidium should be confirmed by the spectroscope (§ V, *a*).

**§ IV. Gravimetric Determination.** — (*a*) In pure solutions, either metal is usually weighed as the neutral sulphate, obtained by evaporation to dryness with sulphuric acid and ignition with ammonium carbonate to constant weight. Rubidium or cæsium may also be weighed as chloride or chloroplatinate. In every case the operations are conducted as for the determination of potassium.

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[1] *I.e.* about 0·54 per cent. This solution is prepared by slow addition of 100 ml. of 95 per cent. alcohol to 20 ml. of 5 per cent. ammonium sulphate solution. The precipitate is filtered off, and the filtrate kept for use with the addition of a few crystals of ammonium sulphate.

(*b*) If only two alkali metals are present in the solution, and both in substantial proportions, the indirect method is applicable (§ III, *b*, 1).

(*c*) Rubidium in presence of potassium: § III, *d*, 4.

(*d*) Cæsium in presence of rubidium and potassium: § III, *d*, 3.

§ **V. Detection in Minerals.**—Rubidium and cæsium exhibit the same chemical reactions as potassium, and hence cannot be distinguished from it except by quantitative comparisons. The spectroscope is indispensable for detecting and identifying the two rarer alkali metals.

(*a*) The spectrum of *rubidium*, although characteristic, is very faint and easily obscured by small quantities of other substances. It is therefore necessary to extract and concentrate it as described in § III, *d* before it can be identified easily and definitely. With a small spectroscope, the red rubidium lines are easily confused with those of potassium; the most characteristic lines are two in the blue, so close as to appear as one, about midway between the blue cæsium lines and the violet potassium line.

(*b*) *Cæsium* has two prominent blue lines (4555 and 4593A.), generally appearing as one line. Unless present in small quantities, it may be detected in the original mineral, a small quantity of the powder (mixed with potassium bisulphate and bifluoride if necessary) being brought into the flame on a cylindrical coil of platinum wire. In most mineral substances cæsium will be looked for only as a small impurity in the potassium fraction, its detection involving the separations given under § III, *d*.

§ **VI. Determination in Minerals and Rocks.**[1]—This is almost invariably conducted by the method of J. Lawrence Smith for the determination of sodium and potassium.[2] The mixed pure alkali chlorides are then treated as in § III, *d*.

(*a*) *Rubidium*.—As indicated under § III, *d*, 4, the total rubidium is collected from several portions. If only a small quantity is present, as is generally the case, the rubidium will all be with the cæsium, from which it is separated as described under § III, *d*, 3. If, however, more than 0·0054 g. of rubidium chloride is present, some of it will remain with the potassium chloride and require repeated extractions until no more is obtained.

(*b*) *Cæsium in Pollucite*.[3]—The mineral is opened up by J. Lawrence Smith's method. The pure mixed alkali chlorides are weighed and precipitated with chloroplatinic acid, the precipitate consisting normally of almost pure cæsium salt. It may be subjected to fractional crystallization from hot water (§ III, *c*, 1), a little potassium being thus obtained.

§ **VII. Complete Analysis of Minerals.**—As mentioned under **V**, § VIII, this involves the determination of silica and common bases in one portion by fusion with sodium carbonate, and of the alkalis in another portion as described under § III, *d*.

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[1] Determination in mineral waters: L. Fresenius, *Zeitsch. anal. Chem.*, 1931, **86**, 182; abstract: *Analyst*, 1931, **56**, 834.

[2] Hillebrand and Lundell, *op. cit.*, p. 788.

[3] R. C. Wells and R. E. Stevens, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 236.

## VII.—BERYLLIUM.

§ I. **Minerals.**—(*a*) *Silicates.*—(1) *Phenacite*, beryllium silicate, $Be_2SiO_4$, crystallizes in transparent to translucent rhombohedral prisms with a vitreous lustre and conchoidal fracture; colour: brown, pale yellow, pale rose, or colourless. H. 7; sp. gr. 3·0.

(2) *Bertrandite*, beryllium hydrogen silicate, $Be_4H_2Si_2O_9$; transparent, vitreous yellow tables often twinned, orthorhombic; cleavage perfect. H. 6·5; sp. gr. 2·6.

(3) *Trimenite*, beryllium manganese silicate, $BeMnSiO_4$; pale pink to colourless, triclinic tabular prisms. H. 6·5; sp. gr. 3·4.

(4) *Beryl*, beryllium aluminium silicate, $Be_3Al_2Si_6O_{18}$; vitreous, transparent to translucent, hexagonal prisms; brittle, uneven fracture; colours: green, pale blue, yellow, white or pale rose. H. 8; sp. gr. 2·7.

(5) *Euclase*, hydrous beryllium aluminium silicate, $2BeO.Al_2O_3.2SiO_2.H_2O$; transparent, pale green, brittle, monoclinic prisms. H. 7; sp. gr. 3·0.

(6) *Leucophanite*, beryllium calcium sodium fluosilicate, $BeCaNaFSi_2O_6$; pale green, transparent, orthorhombic tables; vitreous lustre, brittle; cleavage perfect. H. 4; sp. gr. 2·9. On being heated or struck it shows a bluish luminescence.

(7) *Meliphanite*, another fluosilicate, $Be_2Ca_2NaFSi_3O_{10}$; tetragonal, usually found massive or in obtuse octahedral crystals; colour: yellow to red.

(8) *Helvite* $(Be,Mn,Fe)_7Si_3O_{12}S$, and *danalite* $(Be,Mn,Fe,Zn)_7Si_3O_{12}S$, are complex beryllium manganese iron zinc sulphides and silicates; colours: yellow, brown, green or grey; translucent, brittle minerals with vitreous lustre. Isometric, usually occurring in tetrahedra. H. 6; sp. gr. 3·3.

(*b*) *Other Minerals.*—(1) *Chrysoberyl*, beryllium aluminate, $BeAl_2O_4$; brittle, translucent to transparent, green orthorhombic crystals, often twinned; vitreous lustre, nearly perfect cleavage. H. 8·5; sp. gr. 3·3.

(2) *Beryllonite*, beryllium sodium phosphate, $BeNaPO_4$; occurs in transparent, orthorhombic, colourless to pale yellow prisms, with a brilliant vitreous lustre and perfect cleavage. H. 5·5; sp. gr. 2·8.

(3) *Herderite*, beryllium calcium fluophosphate, $BeCaFPO_4$; yellowish to greenish-white short hexagonal pyramids and prisms; translucent, with sub-conchoidal fracture and vitreous lustre. H. 5; sp. gr. 3·0.

(4) *Hambergite*, basic beryllium borate, $4BeO.B_2O_3.H_2O$; greyish-white, translucent orthorhombic prisms, vitreous lustre, perfect cleavage. H. 7·5; sp. gr. 2·3.

§ II. **Properties and Compounds.**—(*a*) The *metal* is obtained by electrolysis of the double sodium fluoride. It is of a bright silver-white colour, melts at 1278° C., and becomes superficially coated with oxide when heated in the air. The fine powder burns on being heated, forming the oxide, and is readily soluble in acids, but does not decompose water even at a red heat. The compact metal is not attacked by cold dilute sulphuric or concentrated nitric acid, and dissolves only slowly when heated. Sp. gr. 1·93.

(*b*) The *oxide*, BeO (beryllia), is an amorphous white powder (sp. gr. 3·02), which by fusion in the electric furnace becomes harder than ruby, denser and crystalline. After strong ignition it is insoluble in dilute acids. It may be prepared by ignition of the hydroxide, nitrate, carbonate, or sulphate. Not attacked by molten sodium carbonate.

(*c*) The *hydroxide*, $Be(OH)_2$, is thrown down as a gelatinous white precipitate on the addition of alkalis to solutions of its salts. It is insoluble in ammonia, but is soluble in caustic alkalis, alkali carbonates, and ammonium carbonate.

(*d*) The *chloride*, $BeCl_2.4H_2O$, deliquescent crystals yielding basic salts when heated.

(*e*) The *carbonates*: basic salts are precipitated on the addition of alkali carbonates to a cold solution of a beryllium salt. These are soluble in excess of the precipitant, but are reprecipitated on boiling.

(*f*) The *tannin complex* is quantitatively precipitated from beryllium (including tartrate) solutions by a large excess of tannin and a moderate excess of ammonia; a voluminous, flocculent, colourless precipitate readily soluble in dilute acetic or mineral acids.

§ **III. Quantitative Separation.**—Until quite recently the monograph of C. L. Parsons, entitled *The Chemistry and Literature of Beryllium* (Easton, Pa., 1909), was still the most authoritative work on beryllium analysis. During the past twenty years, however, the analytical chemistry of beryllium has undergone most drastic changes, all the more important separation methods described *below* having been published since the appearance of Parsons' book.

Since beryllium is precipitated from solution by ammonia in the same manner as aluminium, its determination in minerals, etc. hinges on its separation from the other constituents of the ammonia precipitate, and particularly from aluminium, its most common mineral associate, as well as its closest relative in chemical deportment.

(*a*) *From Metals of the Hydrogen Sulphide Group.*[1]—Beryllium is not precipitated as sulphide; hence, like aluminium, it can be separated, by treatment of the acid solution with hydrogen sulphide, from members of the copper and arsenic subgroups with the exception of tin, the sulphide of which (according to L. Moser and F. List [2]) adsorbs beryllium. Hence they recommend the following separation procedure. The boiling, strongly acid chloride solution is treated with 5 ml. of 10 per cent. tannin solution, 10 to 20 g. of ammonium acetate, and the same quantity of ammonium nitrate. Flocculation of the tannin precipitate is gradual and becomes complete by digestion on a steam-bath. The precipitate is collected and washed with hot ammonium acetate solution containing a little tannin. If the quantity of tin present exceeds 0·2 g., the precipitate should be dissolved in hot, fairly strong hydrochloric acid, and the precipitation repeated. The precipitate is washed free from chlorides, ignited over a blast-burner, and weighed as $SnO_2$. The beryllia is recovered from the tannin filtrate by ammonia precipitation (§ IV, *b*).

(*b*) *From Aluminium.*—The method at present recommended in the literature is based upon the precipitation of aluminium by 8-hydroxyquinoline. We give preference to fusion of the mixed oxides with sodium carbonate, in the more usual case where alumina preponderates; when, however, beryllia preponderates, we apply the tannin process.

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[1] Copper may be separated from beryllium by electrolysis.

[2] *Monatsh.*, 1929, **51**, 181.

(1) *Hydroxyquinoline method* (I. M. Kolthoff and E. B. Sandell[1]). Aluminium is precipitated in feebly acid acetate solution as $(C_9H_6ON)_3Al$. The reagent is a 5 per cent. solution of the finely powdered base in 2N. acetic acid. The slightly acid solution, containing not more than 0·1 g. of either oxide in 100 ml., is treated at 50° C. with an excess of the reagent. A 2N. ammonium acetate solution is added until a permanent precipitate is obtained, when a further addition of 20 to 25 ml. will complete the precipitation. After settling, the precipitate is collected in a porous glass or porcelain crucible, washed with cold water, dried at 120° to 140° C., and weighed. (Factor for $Al_2O_3$ : 0·1110; for Al : 0·0587.)

The filtrate containing the beryllium is heated nearly to boiling and a faint excess of ammonia is cautiously added. The yellow to brown precipitate is collected and well washed with a hot dilute solution of ammonium acetate containing a few drops of ammonia. It is then dried over a low flame in a tared platinum crucible, ignited over a blast-burner, and weighed as BeO. The weighing must be done with dispatch, as the beryllia is slightly hygroscopic.

Kolthoff and Sandell state that the alumina figures are slightly low and the beryllia results correspondingly high. The crucial point of the method is evidently the neutralization of the solution prior to addition of the reagent. This should be effected by dropwise addition of dilute ammonia until a faint cloudiness is observed, which must be removed with a minimum of acid. It may be advisable to test the recovered beryllia for alumina by the tannin method (2, *below*).

The disadvantage of the hydroxyquinoline process from a practical point of view lies in the fact that it is limited to relatively small quantities of alumina (*cf.* 3, *below*).

(2) *Beryllia preponderates: tannin method.* The separation by means of tannin in acetate solution was first proposed by L. Moser and M. Niessner.[2] The procedure does not appear to have been adopted in practice; it has been criticized by A. D. Mitchell and A. M. Ward,[3] who did not obtain satisfactory separations by its use. As a result of our experience in the analysis of beryl, we share the views of Mitchell and Ward. However, for the separation of small quantities of alumina from beryllia (*e.g.* in testing the purity of beryllium precipitates), tannin is a most valuable reagent.

The hot sulphate solution (200 to 300 ml.), obtained by solution of a bisulphate melt of the mixed oxides containing less than 0·02 g. of alumina, is neutralized with dilute ammonia till just turbid, cleared with a slight excess of acid, and treated with 10 g. each of ammonium acetate and chloride. The boiling solution is precipitated with a freshly prepared solution of 0·5 to 1 g. of tannin. If no precipitate is formed, a few drops of 10 per cent. ammonia should be added in order to induce flocculation; if, on the other hand, the precipitate appears unduly bulky, indicating incipient precipitation of the beryllium complex, the boiling liquid should be treated with 50 per cent. acetic acid added gradually, and the effect noted. The aluminium complex is of a pale buff colour and flocculates readily in the hot solution. After being allowed to settle on the water-bath, it is mixed with filter-pulp, collected, washed with dilute ammonium chloride solution containing a little tannin, and weighed as $Al_2O_3$ after ignition over a blast-burner. The purity of the precipitate may be ascertained by sodium carbonate fusion (3, *below*).

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[1] *J. Amer. Chem. Soc.*, 1928, **50**, 1900.

[2] *Monatsh.*, 1927, **48**, 113.

[3] *Modern Methods in Quantitative Chemical Analysis*, London, 1932, p. 43.

The tannin precipitation of aluminium is applicable in neutralized solutions containing tartaric acid.[1] The separation of the two earths by tannin is inconvenient, if not unreliable, when applied to mixtures high in alumina, on account of the extreme bulkiness of the aluminium-tannin complex.

(3) *Alumina preponderates: sodium carbonate fusion.* This simple and reliable method is due to M. Wunder and P. Wenger.[2] It is based on the fact that alumina reacts with molten sodium carbonate with formation of soluble aluminate whilst beryllia remains unaffected. H. T. S. Britton [3] found that the method yields satisfactory separations in a single fusion when not more than 0·15 g. of either oxide is present.

The mixed oxides are fused with sodium carbonate (5 g. or more) in a covered platinum crucible at a temperature slightly above the melting-point of the salt. The crucible is cautiously swirled from time to time; if this motion is overdone, the suspended oxides adhere to the sides of the crucible above the level of, and out of contact with, the fluid mass. Wunder and Wenger prescribe 2 to 3 hours' fusion, but if the oxides are finely divided (*e.g.* obtained by ignition of precipitates mixed with filter-pulp) a little more than an hour suffices.

The cooled melt is extracted with 250 to 400 ml. of boiling distilled water in a porcelain or platinum capsule. The insoluble residue is allowed to settle, collected on a close-textured filter containing a pad of filter-pulp in its apex, washed with hot water, ignited wet in a tared platinum or silica crucible over a blast-burner, and weighed as BeO. The alkaline filtrate is acidified with nitric acid, boiled until carbon dioxide is expelled, and precipitated with a faint excess of ammonia; the precipitate is converted into and weighed as $Al_2O_3$.

Wunder and Wenger recommend retreatment of the beryllia by the same process as a test for complete separation. With that object in view they ignite the first beryllia residue in a platinum crucible. We prefer, however, to test the beryllia for alumina by the tannin method (2, *above*) for the following reason. Since beryllia itself is not affected by molten sodium carbonate, an oxide mixture in which beryllia largely predominates is not broken up by the flux; hence the small amount of alumina, being surrounded and protected by the inert oxide, may escape attack. We therefore ignite the beryllia residue from a single carbonate fusion in a silica crucible, and fuse the weighed oxide with bisulphate, etc., as detailed under (2), *above*.

It will be seen that tannin precipitation and sodium carbonate fusion are converse methods for the separation of beryllia from alumina.

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[1] W. R. Schoeller and H. W. Webb, *Analyst*, 1929, **54**, 709.

[2] *Zeitsch. anal. Chem.*, 1912, **51**, 470.

[3] *Analyst*, 1922, **47**, 54.

(*c*) *From Iron.*—(1) *Ferrous sulphide method.* The acid chloride or sulphate solution is treated with ammonium chloride, 2 to 4 g. of tartaric acid, and hydrogen sulphide until the ferric salt is reduced to ferrous with separation of sulphur. Ammonia and ammonium sulphide are then added to precipitate the iron as ferrous sulphide. The method is identical with the classic process devised by Berzelius for the separation of aluminium from iron, and is of general applicability to the separation of iron and other sulphide-forming metals from any earth or earths.

The tartrate filtrate containing the beryllium is evaporated with sulphuric, and excess of nitric, acid to destroy the ammonium chloride and tartaric acid. After cooling and dilution, the beryllia is precipitated with ammonia and a little tannin, and the precipitate is ignited in a platinum crucible and fused with sodium carbonate (§ IV, *c*).

If the absolute quantity of beryllia is not excessive (less than 0·02 g.), the tartaric acid need not be destroyed.[1] The tartrate filtrate is acidified with hydrochloric acid, boiled free from hydrogen sulphide, treated with 10 to 20 g. of ammonium chloride, 5 g. of ammonium acetate, and ammonia in moderate excess (2 to 3 ml.), diluted to 250 ml., boiled, and precipitated with 0·5 to 1 g. of tannin (freshly made solution). After short boiling, the liquid is allowed to cool to room temperature, and is filtered under gentle suction after some hours' standing. The bulky precipitate is washed with slightly ammoniacal 2 per cent. ammonium nitrate solution containing a little tannin, and ignited in a platinum crucible. The ignited beryllia is fused with sodium carbonate, etc. (§ IV, *c*).

(2) *Hydroxyquinoline method.* The method for the separation of aluminium from beryllium, described *above* under (*b*, 1), can be used for the separation of beryllium from ferric iron. The iron precipitate is black.

(3) *Tannin method.* Very small amounts of ferric iron may be separated from beryllium by means of tannin, as described *above* under (*b*, 2).

(4) *Iron preponderates: ether process.* For the separation of beryllium from large quantities of iron (*e.g.* in steel analysis), Rothe's ether extraction method is applied. The bulk of the ferric chloride is thus obtained in the ethereal extract, beryllium chloride and a small balance of iron in the aqueous layer. The latter is freed from ether by evaporation, and the separation is completed by method (1) or (2).

For a critical survey of the various methods for the determination of beryllium in complex alloy steels, reference should be made to a paper by L. Fresenius and M. Frommes.[2]

(*d*) *From Aluminium and Iron.*—This separation case deserves special mention, being of practical interest in the analysis of beryl, rocks, etc., in which beryllium is associated with aluminium and small to substantial amounts of iron.

The hydroxyquinoline method of Kolthoff and Sandell (*b*, 1, *above*) is advocated by H. Fischer and G. Leopoldi.[3] It offers the advantage of separating beryllium from iron and aluminium in one operation, but is unsuitable for materials high in aluminium and iron and low in beryllium (*e.g.* rocks) on account of the bulkiness of the precipitate, which limits the quantity of sample to about 0·5 g.

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[1] W. R. Schoeller and H. W. Webb, *Analyst*, 1936, **61**, 236.

[2] *Zeitsch. anal. Chem.*, 1932, **87**, 273; abstract: *Analyst*, 1932, **57**, 270.

[3] *Wiss. Veröff. Siemens Konzern*, 1931, **10**, 3.

It has been shown by V. M. Zwenigorodskaia and T. N. Smirnowa [1] that the addition of 0·2 g. of oxalic acid in the precipitation of aluminium by hydroxyquinoline, prescribed by Fischer and Leopoldi [2] and by Fresenius and Frommes,[2] is not only unnecessary but harmful, as oxalic acid forms a soluble aluminium complex, with resultant high beryllium results.

The older procedure of C. L. Parsons and S. K. Barnes [3] may be said to have outlived its usefulness. It consists in boiling the neutralized solution of the ammonia precipitate with 10 g. of solid sodium bicarbonate per 100 ml. of solution. After boiling for one minute, the solution is cooled and filtered, the filtrate containing most of the beryllia; the precipitate must be dissolved and retreated. Hillebrand and Lundell [4] observe that " some beryllium is always carried down with the aluminium." It is equally certain, however, that a little aluminium finds its way into the beryllium filtrate. By a compensation of errors, tolerably good results may be obtained with materials high in beryllium. Phosphoric acid interferes, beryllium phosphate being precipitated.

The technique used by us in determining beryllium in beryl and rocks is explained in § VII, (*a*) and (*b*).

(*e*) *From Chromium.*—(1) The mixed oxides are fused with sodium carbonate, with addition of a little potassium nitrate if much chromium is present. Extraction with water and filtration gives a filtrate containing chromate and an insoluble residue of beryllia.

(2) In solution, chromic salt is oxidized to chromate by the well-known persulphate method, silver nitrate being used as a catalyst.[5] The beryllia is precipitated by ammonia.

(*f*) *From Titanium.*—(1) *Tannin method.* (*α*) *Authors' method.* When titania is precipitated by tannin from a nearly neutralized oxalate solution half-saturated with ammonium chloride,[6] a quantitative separation of titania from beryllia is achieved in one operation.[7] (For working details, see **XIII,** § III, *d.*)

(*β*) *L. Moser and J. Singer's method.*[8] The cold sulphate solution is neutralized with ammonia until slight opalescence sets in; it is then treated with 10 g. of ammonium acetate, 20 g. of ammonium nitrate, and 20 ml. of acetic acid. The liquid is heated to boiling, and precipitated with 10 times as much tannin as the titania judged to be present. After a few minutes' boiling, the red precipitate is left to settle, collected, washed with 10 per cent. acetic acid containing a little ammonium nitrate, and ignited to $TiO_2$. The beryllium is precipitated as tannin complex in the filtrate with more tannin and an excess of ammonia (§ IV, *b*).

(2) *Cupferron method.* Titanium is precipitated by cupferron (see

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[1] *Zeitsch. anal. Chem.*, 1934, **97**, 323.

[2] *Loc. cit.*

[3] *J. Amer. Chem. Soc.*, 1906, **28**, 1589.

[4] *Op. cit.*, p. 405.

[5] *Ibid.*, p. 411.

[6] W. R. Schoeller and A. R. Powell, *Analyst*, 1932, **57**, 551.

[7] W. R. Schoeller and H. W. Webb, *ibid.*, 1936, **61**, 238.

[8] *Monatsh.*, 1927, **48**, 673.

**XIII,** § III, *e*) from cold, acid solution in presence or absence of tartaric acid.

(3) Minute quantities of titania may be determined colorimetrically in presence of beryllium (see **XIII,** § VI).

(*g*) *From Zirconium.*—(1) The nitrate solution is digested on the water-bath with an excess of caustic soda. The zirconium is precipitated as hydroxide, whereas beryllium dissolves. If much zirconium is present, the precipitate must be dissolved and reprecipitated. The acidified beryllium filtrate is boiled until carbon dioxide is expelled, and precipitated with a slight excess of ammonia and a little tannin (§ IV, *a*, *below*).

(2) Zirconium is precipitated as phosphate (**XIV,** § III, *e*).

(3) The tannin method of Moser and Singer for the separation of titanium from beryllium (*f*, 1, *above*) is applicable, zirconium being precipitated as the white tannin complex.

(4) Cupferron (*f*, 2, *above*) precipitates zirconium as well as titanium.

(*h*) *From Uranium.*—*Ferrocyanide method.*[1] This has the advantage over other methods that it can be applied in sulphate solution. The cold solution (100 ml. per 0·1 g. $U_3O_8$) is treated with 2 g. of ammonium chloride, a cream of filter-pulp, and a solution of 0·3 g. of potassium ferrocyanide, the precipitate being blended with the fibre by vigorous stirring. After one hour the precipitate deposits completely, provided that enough pulp has been added. The liquid is filtered through close-textured paper; the pulp containing the red uranyl ferrocyanide is returned to the beaker with cold 2 per cent. ammonium chloride solution, stirred up, returned to the filter, and the washing is completed. The beryllium in the filtrate is precipitated hot with ammonia and a little tannin; the precipitate is collected, washed with ammonium chloride solution, ignited in a platinum crucible, and fused with sodium carbonate, etc., as described under § IV, *c*. The weighed beryllia may contain a fraction of a mg. of ferric oxide; it is therefore fused with bisulphate, and the iron determined colorimetrically.

The filter containing the ferrocyanide precipitate is returned to the beaker, and destroyed with nitric and sulphuric acids (see **XXII,** § III, *j*).

(*i*) *From Thorium.*—(1) By sodium hydroxide: as for zirconium (*g*, 1, *above*).

(2) By oxalic acid: see **XV,** §§ III and IV.

(*j*) *From Rare Earths.*—See **XII,** § III, *a*.

(*k*) *From Phosphoric Acid.*—This is accomplished by fusion with sodium carbonate and extraction of the melt with water. Sodium phosphate goes into solution; beryllia remains insoluble.

(*l*) *From Vanadium.*—As in the preceding case, fusion with sodium carbonate furnishes soluble sodium vanadate and insoluble beryllia.

§ **IV. Gravimetric Determination.**—Beryllium is always weighed as the oxide, BeO, obtained by strong ignition of the hydroxide, the tannin complex, or the residue from a sodium carbonate fusion.

(*a*) *Precipitation of the Hydroxide.*—The precipitation is carried out in a similar manner to that of alumina, by addition of a feeble excess of ammonia to the hot solution of the chloride or nitrate free from other metals, and containing ammonium salt. An excess of ammonia exerts a solvent action upon the precipitate. L. Moser and J. Singer[1] find the solubility of beryllium hydroxide to equal 0·002 g. of BeO per litre of water, 0·0045 g. for aqueous 1 per cent. ammonia, and 0·003 g. for 1 per cent. ammonium chloride *plus* 0·1 per cent. ammonia. The precipitation should be carried out in presence of an indicator, such as methyl red or a piece of litmus-paper. The precipitate is allowed to settle, mixed with creamed filter-pulp, collected, washed with warm 2 per cent. ammonium nitrate, and ignited wet in a tared platinum or silica crucible. It should be ignited at 1000° C., and weighed quickly in the covered crucible, as it is rather hygroscopic.

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[1] W. R. Schoeller and H. W. Webb, *Analyst*, 1936, **61**, 240.

The filtrate should be tested for complete recovery of the beryllia. This may be done by acidifying the solution, boiling it down, and readjusting it to slight alkalinity, but we prefer adding a few ml. of 1 per cent. tannin solution to the slightly ammoniacal liquid, which at once coagulates any trace of beryllia, with formation of an opaque flocculent precipitate. The tannin may with advantage be added in the original precipitation, as it counteracts the solvent effect of ammonia.

Contrary to statements in the literature, no loss of beryllia takes place during ignition of an ammonia precipitate washed with ammonium chloride solution; beryllium chloride solutions can be converted into beryllia by simple evaporation, and ignition of the residue.[2] Similar conclusions have previously been reached in the case of alumina.

(*b*) *Precipitation of the Tannin Complex.*—(1) L. Moser and J. Singer[1] recommend tannin precipitation for minute quantities of beryllium on account of the voluminous nature of the precipitate. The feebly acid solution, containing no other metals except alkalis, is treated with 20 to 30 g. of ammonium nitrate and, while boiling, with 10 times as much tannin as the beryllia present, and finally with dilute ammonia drop by drop until precipitation is complete. We recommend fusion of the ignited precipitate with sodium carbonate (*c, below*).

(2) W. R. Schoeller and H. W. Webb[3] have shown that beryllium can be directly recovered by tannin precipitation from tartrate solution (*e.g.* the filtrate from ferrous sulphide precipitated in ammoniacal tartrate solution), which obviates destruction of the tartaric acid. The manipulation is described under § III, *c*, 1.

We do not advocate the above procedure in preference to other methods for the determination of beryllium; it is, however, a useful and rapid method for the recovery of small quantities. Tannin precipitations from ammoniacal solutions are less elegant than those from neutral or slightly acid ones; the ammoniacal liquor gradually darkens through oxidation, and contamination of the precipitate with silica from the glass vessels is appreciable. The ignited tannin precipitate should be purified by the process given *below.*

(*c*) *After Sodium Carbonate Fusion.*—The determination of beryllium by precipitation with ammonia is subject to positive errors, due to coprecipitation of alkali. Hillebrand and Lundell[4] prescribe double or triple precipitation in presence of sodium chloride (*e.g.* in silicate analysis). Care has to be exercised to prevent loss of beryllium in these repeated manipulations (*cf. a, above*). Again, if precipitated in sulphate solution, beryllium hydroxide carries down considerable sulphur trioxide, the expulsion of which requires a temperature of 1200° C., whilst an excess of ammonia in reprecipitation causes low results. Bisulphate fusions, however, are frequently required in mineral analysis, hence a method must be available for the determination of beryllium in sulphate solution. Schoeller and Webb [1] have adopted fusion of the ignited ammonia or tannin precipitate with sodium carbonate and extraction of the fused mass with water (Wunder and Wenger's process, § III, *b*, 3), which furnishes a residue of purified beryllia in a weighable form. The procedure removes sulphur trioxide, adsorbed alkali, and traces of impurities such as alumina and silica.

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[1] *Loc. cit.*

[2] L. Fresenius and M. Frommes, *Zeitsch. anal. Chem.*, 1933, **93**, 275.

[3] *Analyst*, 1936, **61**, 237.

[4] *Op. cit.*, p. 406.

The crude beryllia precipitate is fused with 2 to 5 g. of sodium carbonate in a platinum crucible for an hour at low temperature, and the cold melt is extracted with 100 to 300 ml. of hot water in a porcelain basin. The insoluble oxide is collected on a close-grained filter containing a pad of filter-pulp, washed with hot water, ignited strongly, and weighed as BeO.

§ **V. Colorimetric Determination.**—A rapid colorimetric process applicable to beryl, etc. has been worked out by H. Fischer.[2] It utilizes 1,2,5,8-tetrahydroxyanthraquinone (quinalizarin), which yields a bright cornflower-blue lake with alkaline beryllate solutions. The alkaline solution of the reagent has a violet colour which is not affected by the presence of alkali aluminate.

Solutions required: (1) pure beryllium nitrate in 0·25N. sodium hydroxide (0·1 g. BeO per litre); and (2) a freshly made, 0·05 per cent. solution of the dye in 0·25N. sodium hydroxide.

Standardization of the dye solution: (*a*) 10 ml. is transferred to a conical flask and diluted to 200 ml. with 0·25N. sodium hydroxide.

(*b*) Another 10 ml. of dye solution is treated with excess of standard beryllium solution, and diluted to 200 ml. with 0·25N. sodium hydroxide. The blue solution serves as a colour standard.

Solution (*a*) is next titrated with standard beryllium solution, a sample being transferred to a colorimeter after each addition, and compared with a sample of solution (*b*), the sample of (*a*) being returned to the bulk before the next addition. The titration is carried on until the tint of (*a*) matches that of the colour standard (*b*).

(*c*) The unknown beryllium solution in 0·25N. alkali is added to 10 ml. of dye solution, diluted to 200 ml. with 0·25N. alkali, and matched against solution (*b*) in exactly the same manner as (*a*). A smaller volume of standard beryllium solution is required in this titration to equalize the tints, the difference between the two readings giving the quantity of beryllia in the unknown solution.

For the determination of beryllia in beryl, the finely powdered mineral (0·2 g.) is fused with sodium carbonate, etc., for the separation of silica by the usual method. The filtrate from the silica is neutralized with sodium hydroxide and diluted to 200 ml. with 0·25N. alkali. The small quantity of ferric hydroxide is left to settle, and an aliquot volume of the clear liquor treated as under (*c*), *above*. The results, whilst necessarily approximate, are serviceable.

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[1] *Analyst*, 1936, **61**, 237.

[2] *Zeitsch. anal. Chem.*, 1928, **73**, 54.

§ **VI. Detection in Minerals.**—The mineral (usually a silicate) is decomposed by fusion with sodium carbonate, the melt disintegrated with hot water, and the acidified solution evaporated to dryness. The dry residue is digested with hydrochloric acid, and the insoluble matter filtered off. Acid-soluble materials are attacked with appropriate acids. The solution is freed from heavy metals, if present, by treatment with hydrogen sulphide. The filtered solution is boiled with nitric acid, nearly neutralized with sodium hydroxide, evaporated to small bulk, and poured gradually into an equal volume of hot 20 per cent. sodium hydroxide solution. The liquid is filtered, acidified with hydrochloric acid, boiled free from carbon dioxide, and treated with a very slight excess of ammonia. If no precipitate is obtained, then beryllium is absent. If the reverse is the case, the precipitate is mixed with filter-pulp, collected, washed with ammonium chloride solution, ignited in a platinum crucible, and fused with sodium carbonate. The residue (if any) from the extraction of the fusion with water should consist of substantially pure beryllia, answering the following tests after fusion with bisulphate and solution in water:

(*a*) The solution gives with ammonium carbonate solution a white precipitate, readily soluble in excess of the precipitant. When boiled, this solution is reprecipitated.

(*b*) The boiling solution is treated with ammonium nitrate, tannin, and a slight excess of dilute ammonia. The voluminous white precipitate formed is readily soluble on reacidification with acetic acid.

(*c*) The solution gives with caustic soda a white gelatinous precipitate, soluble in excess.

(*d*) The alkaline solution from (*c*) gives with quinalizarin reagent (*cf.* § V) a fine cornflower-blue solution.

§ **VII. Determination in Minerals.**—(*a*) *Beryl and Other Silicate Minerals.*—Finely powdered beryl (0.5 g.) is fused in platinum with 5 g. of sodium carbonate. The determination is conducted by the standard process of silicate analysis to the stage where the ammonia precipitate has been collected, the residue from the volatilization of the silica having been fused with a little bisulphate and added to the main filtrate prior to precipitation with ammonia. The precipitate is dissolved in dilute hydrochloric acid, the solution is neutralized as closely as possible, and the determination is carried out by the hydroxyquinoline method described under § III, *b*, 1.

Alternatively, the ignited ammonia precipitate is fused with 5 g. of sodium carbonate, and the aluminate extracted by lixiviation with water (§ III, *b*, 3). The residue is strongly ignited in a tared silica crucible, weighed, fused with potassium bisulphate, and the melt dissolved in acidulated water. Iron and any traces of residual aluminium may be precipitated together by tannin (§ III, *b*, 2) or hydroxyquinoline (§ III, *d*). The weight of the mixed oxides, being deducted from that of the sodium carbonate fusion residue, gives the beryllia by difference.

(*b*) *Rocks.*—The determination of beryllia in rocks has become a subject of scientific, if not of commercial, interest. Beryllia has never yet been reported in petrographic work, although beryl is a frequent minor constituent of pegmatites and certain igneous (sodic) rocks. Hillebrand and Lundell[1] express the opinion that "it should be the duty of every petrographic analyst to make a special search for beryllium."

As for the procedure to be followed in this search, no standard method has as yet been adopted. Fischer and Leopoldi[2] condemn Parsons and Barnes' bicarbonate process (§ III, *d*) as it indicated one or more units per cent. in a pegmatite containing 0·01 per cent. of beryllia, the "beryllium" fraction obtained in the process being found to consist of alumina, silica, and ferric oxide. The same authors use the hydroxyquinoline method for the determination, but as the absolute quantity of alumina and ferric oxide present militates against the direct application of the method, they remove the alumina by Havens' ether method,[3] based on the fact that aluminium chloride is sparingly soluble in ether saturated with hydrogen chloride. In this rather unattractive procedure the aluminium chloride may have to be reprecipitated once or twice, while the beryllium fraction still contains aluminium.

In searching for small amounts of beryllia in rocks, we definitely favour Wunder and Wenger's method (§ III, *b*, 3) for the removal of alumina from the ammonia precipitate. Large quantities of material can thus be worked up in several portions, and if the removal of the alumina is incomplete in one operation, the fusion can still be repeated on the extracted residues. B. E. Dixon[4] also applies this step, by fusing the ammonia precipitate with 5 g. of sodium carbonate for 2½ to 3 hours at low temperature, and digesting the melt with 500 ml. of water overnight.

The fusion process removes any chromium, vanadium, phosphorus, and small amounts of silica as well as the alumina. Manganese, if present, is detected by the greenish colour of the cooled carbonate melt.

The extracted residue from the carbonate fusion is fused with potassium bisulphate, the solution precipitated with hydroxyquinoline, and the beryllium recovered from the filtrate by ammonia (§ III, *b*, 1).

Alternatively, the unignited ammonia precipitate may be dissolved in hydrochloric acid, and the hot solution, after approximate neutralization with caustic soda, slowly poured into hot 10 per cent. sodium hydroxide solution during continuous agitation. The precipitate is collected, washed twice, dissolved, and the precipitation is repeated. The combined filtrates are acidified, boiled until free from carbon dioxide, and precipitated with a faint excess of ammonia. The precipitate (alumina and beryllia) is collected, washed, ignited in platinum, and fused with sodium carbonate. The melt is extracted with water, beryllia remaining in the insoluble residue.

However obtained, the final beryllia should be identified as such (§ V).

(*c*) *Phosphates.*—0·5 to 1 g. of finely powdered mineral is fused with 4 to 5 g. of sodium carbonate. The fused mass is taken up in hot water, and the extract, containing the phosphorus as sodium phosphate, is filtered. The residue, containing the whole of the beryllia, is fused with potassium bisulphate; the melt is dissolved in dilute hydrochloric acid, and the filtered solution precipitated with ammonium chloride and ammonia (double treatment). The precipitate is dissolved in dilute hydrochloric acid and the solution treated with hydroxyquinoline, etc. as described under (*a*), *above*.

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[1] *Op. cit.*, p. 402.

[2] *Wiss. Veröff. Siemens Konzern*, 1931, **10**, 3.

[3] *Amer. J. Sci.* (4), 1897, **4**, 111.

[4] *Analyst*, 1929, **54**, 268.

§ **VIII. Complete Analysis.**—The complete analysis of beryllium minerals and beryllium-bearing mineral mixtures (mostly silicates) is carried out by the standard processes of silicate analysis, beryllia accompanying the alumina into the ammonia precipitate. The only additional manipulation required is a determination of beryllium in that precipitate by one of the methods given in the preceding subsection.

## VIII.—SCANDIUM.

§ **I. Minerals.**—(*a*) *Thortveitite*, a silicate of scandia and the yttria earths, $M_2O_3 . 2SiO_2$ (37 per cent. of scandia, 17·5 per cent. of yttria earths), is the only mineral in which scandium is the principal basic constituent. Orthorhombic, grey-green, brittle mineral with brilliant adamantine lustre; twins common. H. 6·5; sp. gr. 3·57.

(*b*) *Wiikite* is a very complex mineral containing 1 to 1·5 per cent. of scandia, together with large amounts of rare earths and earth acids, titania, zirconia, silica, thoria, and oxides of uranium and iron. Black, amorphous, radioactive. H. 6; sp. gr. 4·85.

(*c*) Scandium is found in small quantities in many rare-earth minerals, and in some specimens of mica, cassiterite, and wolfram.

§ **II. Properties and Compounds.**—(*a*) The *metal* has been obtained, in the form of a sintered, light grey mass, by the electrolysis of the molten chloride. Melting-point approximately 1400° C.; density 3·1.

(*b*) The *oxide*, $Sc_2O_3$, is a white powder soluble in hot dilute acids; formed on ignition of a scandium salt of a volatile acid.

(*c*) The *fluoride*, $ScF_3$, is a white gelatinous precipitate, formed by the action of a soluble fluoride or fluorosilicate upon a boiling solution of a scandium salt. Like zirconium, scandium forms soluble double salts with the alkali fluorides; their general formula is $ScF_3 . 3MF$.

(*d*) The *sulphate*, $Sc_2(SO_4)_3 . 7H_2O$, crystallizes in globular aggregates fairly soluble in water. With potassium sulphate it gives a double salt, $Sc_2(SO_4)_3 . 3K_2SO_4$, insoluble in a saturated solution of the precipitant; the corresponding sodium salt, however, is soluble in a saturated solution of sodium sulphate.

(*e*) The *carbonate* is a white precipitate soluble in alkaline carbonates; when the solution is boiled, double salts are precipitated.

(*f*) The *oxalate*, $Sc_2(C_2O_4)_3 . 5H_2O$, is precipitated by oxalic acid from solutions of scandium salts. Slightly soluble in water, readily soluble in ammonium oxalate solution, giving a stable double salt which crystallizes out on evaporation.

§ **III. Quantitative Separation.**—Scandium accompanies the rare-earth metals in analysis, being precipitated with them by addition of oxalic acid to acid chloride, nitrate, or sulphate solutions; scandium oxalate is, however, among the most soluble of the rare-earth oxalates. In the double sulphate separation scandium is precipitated with the ceria earths when potassium sulphate is used as precipitant, but passes into the yttria-earth filtrate when sodium sulphate is used; it is precipitated with thorium when the neutral earth chloride solution is boiled with sodium thiosulphate. Recently G. Beck [1] has found that sodium alizarin-3-sulphonate is a satisfactory precipitant for scandium from solutions containing yttria earths.

(*a*) *From the Ceria Earths.*—This is effected by saturating the warm chloride solution with sodium sulphate and setting the solution aside overnight in a cool place (see **XII**); all the scandium passes into the filtrate with the yttria earths. If much scandium is present in the solution, however, it is better to follow procedure *b*, 1.

(*b*) *From the Yttria Earths.*—(1) The neutral chloride solution is boiled with an excess of sodium thiosulphate, which precipitates all the scandium and thorium as basic thiosulphates. The washed precipitate is extracted with hot dilute hydrochloric acid and the precipitation repeated. The acid extract of the second precipitate is treated as described in (*c*).

(2) The neutral sulphate or chloride solution is treated with 5 g. of ammonium acetate and 0·5 ml. of acetic acid and heated on the water-bath; a 2 per cent. solution of sodium alizarin-3-sulphonate is then added until no further violet precipitate forms. The precipitate is collected, washed with hot 1 per cent. ammonium acetate solution, and dissolved in hydrochloric acid. It may be reprecipitated by addition of ammonium acetate and more of the precipitant. If thorium is present, it is completely precipitated with the scandium.

(*c*) *From Thorium.*[2]—This is best accomplished in two stages: (1) The scandium is separated from the bulk of the thorium by pouring the neutral solution of the chlorides into a large excess of sodium carbonate and boiling the mixture, whereby scandium sodium carbonate is precipitated. The precipitate, which contains about 0·5 per cent. of thoria, is filtered off, washed with hot sodium carbonate solution, and dissolved in hydrochloric acid; the remainder of the thorium is then separated by either of the two following methods:

(2, α) The solution is neutralized with sodium carbonate, avoiding a permanent precipitate, and added drop by drop with constant stirring to a 20 per cent. solution of neutral ammonium tartrate. The resulting clear liquor is boiled with 1 to 2 ml. of ammonia, which precipitates scandium ammonium tartrate; this is filtered off, washed with hot ammonium tartrate solution, and ignited to oxide.

(*β*) The neutral chloride solution is poured with vigorous stirring into a solution of ammonium fluoride containing at least eight times as much salt as there is scandia present. After boiling a short time, the precipitate of thorium fluoride is filtered on a vulcanite funnel, the filtrate evaporated with sulphuric acid to expel hydrofluoric acid, and the scandia precipitated with ammonia or oxalic acid.

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[1] *Mikrochemie*, 1939, **27**, 47.

[2] For these and other methods see Meyer and Winter, *Zeitsch. anorg. Chem.*, 1910, **67**, 398; *Chem. News*, 1910, **102**, 163, 175; Meyer and Goldenburg, *ibid.*, 1912, **106**, 13; Meyer and Wassjuchnow, *Zeitsch. anorg. Chem.*, 1914, **86**, 257; Sterba-Böhm, *Zeitsch. Elektrochem.*, 1914, **20**, 289.

§ **IV. Gravimetric Determination.**—Scandium is weighed as the oxide $Sc_2O_3$, formed by ignition of the oxalate or hydroxide. The former is precipitated like the rare-earth oxalates (see **XII,** § IV), the latter in a similar manner to alumina. Both precipitates may be washed with warm water and ignited wet to constant weight. The oxide is also obtained by ignition of the alizarin-3-sulphonate.

§ **V. Detection in Minerals.**—The mineral is decomposed as described under **XII,** § VI: the precipitated oxalates will contain all the scandium; they should be ignited to oxides, the latter dissolved in acid, and the solution precipitated with sodium sulphate. The filtrate containing yttria earths and scandia is treated as described in § III, *b*, 2, the precipitate ignited to oxide, and the latter dissolved in hydrochloric acid. The arc spectrum of the solution is then examined for the lines 3572·7, 3614·0, 3630·9, 4247·0A., which are highly characteristic of scandium.

For a chemical test the alizarin-3-sulphonate precipitate, which contains all the thoria as well as the scandia, is dissolved in hydrochloric acid, the solution evaporated almost to dryness, diluted somewhat and poured into an excess of boiling ammonium fluoride solution, which precipitates the thoria. The filtrate is evaporated to a low volume and treated with hexamminecobaltic nitrate solution, which produces a characteristic crystalline precipitate of $[Co(NH_3)_6]ScF_6$.

§ **VI. Determination in Minerals.**—(*a*) *In Minerals containing Much Rare Earths.*—The ore is decomposed as described under **XII**, § VII, and the earths separated with sodium sulphate into cerium and yttrium groups. The scandium accompanies the latter, and is separated from these and from thorium as described in § III.

(*b*) *In Wolframite.*[1]—100 g. of the mineral is fused with 230 g. of sodium carbonate, the melt leached with hot water, and the solution filtered. The residue is dissolved in hydrochloric acid and the solution evaporated to dryness. The mass is taken up in dilute hydrochloric acid and the silica removed by filtration; the filtrate is boiled with 3 to 4 g. of sodium fluorosilicate, added with constant stirring, and the boiling continued for half an hour. The insoluble scandium fluoride is filtered off, washed with hot very dilute hydrochloric acid, and dissolved in strong sulphuric acid. The scandium is precipitated from this solution with ammonia, the precipitate dissolved in hydrochloric acid, and the solution treated as described in § III, *b*, 2.

(*c*) *In Thortveitite.*[2]—One g. of finely ground ore is fused with 5 to 6 g. of sodium hydroxide in a silver or nickel crucible at a dull red heat, the melt being stirred with a silver or nickel rod until completely decomposed. After cooling, the product is extracted with hot water, and the residue collected, washed with hot water, and dissolved by heating with concentrated sulphuric acid. The solution of the sulphates in cold water is treated with an excess of ammonia, and the washed precipitate dissolved in nitric acid; the solution is then evaporated to dryness, the nitrates are dissolved in cold water, and the scandium is precipitated by saturating the solution with potassium sulphate. Next morning the precipitate is collected, washed with a saturated solution of the precipitant, and digested with a cold 25 per cent. solution of ammonium carbonate. The filtered liquor, containing the scandium as a double carbonate, is boiled until it ceases to evolve ammonia, and the precipitated basic scandium carbonate is collected, washed with hot water, and dissolved in hydrochloric acid; the solution is treated as described in § III, *b*, 2, the violet sulphonate precipitate being ignited to, and weighed as, $Sc_2O_3$.

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[1] Adapted from Meyer, *Zeitsch. anorg. Chem.*, 1908, **60,** 134; *Chem. News*, 1909, **99,** 85, 97; and Sterba-Böhm, *loc. cit.*

[2] After P. and G. Urbain, *Compt. rend.*, 1922, **174,** 1310.

## IX.—GALLIUM.

§ **I. Minerals.**—Gallium is one of the rarest elements, and no mineral is yet known of which it is an essential constituent. The richest source of gallium is *germanite* (*q.v.*), which contains 0·5 to 0·8 per cent. of the element.

Gallium occurs in traces in many zinc blendes, in a large number of iron ores (*e.g.* magnetite, clay-ironstone, and black-band ore), and in many samples of bauxite and kaolin. In the metallurgical processes carried out for the extraction of zinc, iron, or aluminium, the gallium concentrates in the metal produced, or in certain by-products.

§ **II. Properties and Compounds.**—(*a*) The *metal* is hard, brittle, and of a grey colour with a greenish-blue reflex. It melts at 30·15° C., and has a great tendency to remain in the superfused state. Its sp. gr. at 24·5° C. is 5·96 for the solid and 6·07 for the liquid; hence, like water, it expands on freezing. Gallium is only superficially oxidized in air even at a dull red heat, and dissolves very slowly in any single mineral acid, but readily in *aqua regia*; it dissolves in caustic alkalis with evolution of hydrogen. Prepared by electrolysis from alkaline sulphate solution.

(*b*) The *oxide*, $Ga_2O_3$, is formed by ignition of the nitrate or hydroxide as a white powder insoluble in acids or alkalis after strong ignition, but soluble in fused bisulphate. The *hydroxide* is precipitated by a slight excess of ammonia; it is soluble in caustic potash.

(*c*) The *trichloride*, $GaCl_3$, resembles aluminium chloride, and is formed when the metal is heated in a current of chlorine or hydrogen chloride. It crystallizes in white needles, melts at 75° C., boils at 220° C., and is very deliquescent, giving a solution from which basic chlorides separate on standing.

(*d*) The *sulphate*, $Ga_2(SO_4)_3$, is a white, very soluble crystalline salt, which forms alums with the sulphates of ammonium, potassium, cæsium, rubidium, and thallium (isometric crystals).

(*e*) The *ferrocyanide* is a white amorphous precipitate insoluble in hydrochloric acid (1 : 2 water).

(*f*) The *tannin complex* closely resembles the corresponding aluminium compound.

§ **III. Quantitative Separation.**—The analytical chemistry of gallium has been extensively studied during the last ten years or so, chiefly by American investigators and by L. Moser and his collaborators in Vienna.

Gallium belongs to the third analytical group of metals, and in the ordinary course of an analysis it follows the aluminium, its hydroxide being precipitated by ammonia, and soluble in sodium hydroxide solution. Like titanium and zirconium, however, it gives a compound with cupferron which is insoluble in cold dilute sulphuric acid. Unlike aluminium, but like ferric iron, its chloride is soluble in ether.

(*a*) *From Silver.*—Precipitation of silver from nitrate or sulphate solutions by addition of hydrochloric acid in very slight excess yields a satisfactory separation.

(*b*) *From Metals of the Hydrogen Sulphide Group.*—Gallium is not precipitated by hydrogen sulphide provided that the solution into which the gas is passed contains at least 10 per cent. of sulphuric or hydrochloric acid. Cadmium may be incompletely precipitated under these conditions, but can subsequently be removed as described under (*c*).

(*c*) *From Cadmium, Zinc, Nickel, Cobalt, Manganese, Thallium, and Beryllium.*[1]—The feebly acid solution is treated with 2 per cent. of ammonium nitrate, then with ammonium acetate sufficient to combine with the free mineral acid, and heated to boiling; the gallium is precipitated by addition of a 10 per cent. tannin solution until ten times as much tannin has been added as there is gallia present (minimum: 0·5 g. of tannin). The resulting voluminous precipitate is collected on a No. 41 Whatman filter, washed with 1 per cent. ammonium nitrate solution containing a few drops of acetic acid and a little tannin, dried and ignited, cautiously at first, then more strongly, to $Ga_2O_3$. If much gallium is present, the greater part is precipitated as basic acetate before the tannin is added. If this occurs, the precipitate should be collected, washed with dilute ammonium acetate solution and set aside until the remainder has been recovered by the tannin method; both precipitates are then ignited together. Beryllium may be recovered from the filtrate by addition of ammonia and more tannin, thallium by evaporation with nitric acid to destroy organic matter, followed by precipitation with potassium chromate, and cadmium, zinc, nickel, cobalt, and manganese by precipitation with ammonium sulphide.

(*d*) *From Aluminium, Chromium, Indium, Uranium, and Rare Earths.*[2]—The solution, which should contain not more than 0·3 g. of gallium and all the uranium in the sexivalent form, is evaporated with sulphuric acid to expel nitric and hydrochloric acids, diluted with water, and adjusted to 2N. sulphuric acid; the total volume should be 200 to 300 ml., and the temperature should not exceed 20° C. The gallium is precipitated by addition of a cold 6 per cent. solution of cupferron until no further white flocculent precipitate is formed; after stirring with a little filter-pulp until the precipitate settles well, the liquid is filtered under gentle suction, and the precipitate washed with cold N. sulphuric acid and eventually sucked as dry as possible. The paper and precipitate are transferred to a porcelain crucible and heated gently over an asbestos gauze until organic vapours cease to be evolved; the carbon is then burned off at as low a temperature as possible, and the residual gallia finally ignited at 1000° C. under good oxidizing conditions, cooled and weighed.

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[1] L. Moser and A. Brukl, *Monatsh.*, 1928, **50**, 188.

[2] L. Moser and A. Brukl, *ibid.*, 1929, **51**, 326.

(*e*) *From Iron.*—(1) Small quantities of gallia are separated from large amounts of iron by reducing the iron with hydrogen sulphide, neutralizing the solution with sodium carbonate, adding 10 g. of sodium thiosulphate, and boiling for 15 minutes with the occasional addition of a few ml. of aniline to neutralize the liberated acid. The precipitated gallia is collected, washed well with hot water, and ignited; it always contains a little iron, and is therefore fused with bisulphate, the melt dissolved in hot water, the solution (100 ml.) treated with 20 ml. of 10 per cent. sulphosalicylic acid and ammonia until slightly alkaline, and saturated with hydrogen sulphide to precipitate the iron as sulphide. The filtrate from the ferrous sulphide is acidified with acetic acid and the gallium recovered with tannin as under (*c*), *above*.

(2) Small amounts of iron are separated from large amounts of gallium by precipitation with sodium hydroxide exactly as for the separation of iron from aluminium. Double precipitation of the iron is advisable, although, according to E. H. Swift,[1] one treatment suffices if the final concentration of the alkali is 0·3N. This method also separates titanium and zirconium from gallium.[2]

(3) J. Papish and L. E. Hoag [3] recommend precipitation of iron with $\alpha$-nitroso-$\beta$-naphthol in feebly acid chloride solution to which a slight excess of ammonium acetate has been added. The gallium is best recovered from the filtrate by addition of ammonia and tannin, but, after ignition, should be purified by fusion with bisulphate followed by a second precipitation with tannin from a slightly acid acetate solution.

(*f*) *From Aluminium, Chromium, Manganese, Mercury, Lead, Bismuth, and Thallium.*—The chloride solution is treated with one-quarter its volume of concentrated hydrochloric acid, then with a 5 per cent. solution of potassium ferrocyanide until no further precipitate forms, heated to 60° to 70° C. for 30 minutes, set aside in a cool place overnight, and filtered. The gallium ferrocyanide precipitate is washed with cold 1 : 3 hydrochloric acid, dried, and ignited with 2 g. of ammonium nitrate. The residue is fused with bisulphate and the iron separated with sodium hydroxide (*e*, 2).

(*g*) *From Large Amounts of Aluminium.*—This is accomplished by precipitation of the aluminium as $AlCl_3.6H_2O$ with ether in concentrated hydrochloric acid; for details see § VI, *d*.

§ **IV. Gravimetric Determination.**—(*a*) *As Gallium Oxide.*—Gallium is generally weighed as the oxide $Ga_2O_3$, obtained by ignition of the hydroxide or the tannin complex at 1000° C. Since the oxide is somewhat hygroscopic, the crucible should be covered immediately ignition is finished, and transferred to a desiccator as soon as it has cooled sufficiently; it should also be weighed with the lid on.

(1) *Precipitation with tannin.* This is described under § III, *c*.

(2) *Precipitation with ammonia.* The nitrate solution is treated with

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[1] *J. Amer. Chem. Soc.*, 1924, **46**, 2377.

[2] *Ibid.*, 1928, **50**, 2118.

[3] *Amer. J. Sci.* (4), 1916, **42**, 389.

2 to 3 g. of ammonium nitrate, then with ammonia drop by drop until the solution is just alkaline to cresol red. Addition of a little filter-pulp and boiling assist filtration. An excess of ammonia must be avoided since the precipitate is appreciably soluble; addition of a little tannin overcomes this solubility and facilitates filtration. The precipitate should be washed with 2 per cent. ammonium nitrate solution rendered just alkaline to cresol red by the addition of a drop or two of ammonia. If the solution contains chlorides, care must be taken to wash thoroughly until all trace of chloride is removed, otherwise there is likely to be a loss of gallium as chloride on ignition.

(3) *Precipitation with ammonium bisulphite.*[1] The sulphate solution containing not more than 0·1 g. of gallium in 100 to 200 ml. is made feebly alkaline to litmus by addition of ammonia, and vigorously boiled for five minutes with 10 ml. of a solution of ammonium bisulphite prepared by saturating 1 : 1 ammonia with sulphur dioxide. After cooling somewhat, a drop or two of dilute ammonia is added until the solution is just alkaline to methyl red. The precipitate is collected, washed, and ignited as described *above.* This method affords a precipitate which does not adhere to the walls of the beaker as does that produced by ammonia.

(*b*) *As Gallium 8-Hydroxyquinoline.*[2]—The slightly acid chloride or sulphate solution is treated with 5 g. of ammonium tartrate, then with ammonia until the solution smells faintly, heated to boiling, and precipitated with a 10 to 50 per cent. excess of a 5 per cent. solution of 8-hydroxyquinoline in 2N. acetic acid, more ammonia being added if necessary to keep the solution feebly ammoniacal. The precipitate is collected in a porous glass crucible under gentle suction, washed with hot water, dried at 105° to 120° C. for one hour, cooled, and weighed as $(C_9H_6ON)_3Ga$, which contains 13·88 per cent. Ga.

(*c*) *By Electrolysis.*[3]—The sulphate solution free from ammonium salts is treated with 1 g. of hydrazine sulphate and just sufficient 10 per cent. sodium hydroxide solution to redissolve the precipitate first formed, diluted to 100 ml., and electrolysed in a beaker with a platinum gauze cathode, which has previously been copper-plated and weighed, and a centrally disposed platinum spiral anode. Electrolysis is continued for several hours or preferably overnight using 0·2 to 0·4 amp. The cathode is raised from the solution without switching off the current, rinsed first with warm water, then with alcohol, dried in a vacuum desiccator, and weighed. It must not be heated during drying, since gallium melts at 30° C. The preliminary copper plating is essential as gallium attacks the surface of platinum and cannot be completely removed by treatment with nitric acid.

§ **V. Detection in Ores.**—(*a*) *In Zinc Blende.*—50 to 100 g. of the finely powdered mineral is boiled gently with 300 to 400 ml. of concentrated hydrochloric acid, more acid being added from time to time until no further hydrogen sulphide is evolved; nitric acid is then cautiously added to oxidize the ferrous chloride and dissolve any still unattacked sulphides. When all the mineral is dissolved, the solution is boiled down to a syrup, which is diluted with 800 ml. of hot water and filtered; the filtrate is treated with strips of pure electrolytic zinc until no further metallic sponge is precipitated, filtered, and just neutralized with sodium carbonate. A gallium concentrate is then obtained by boiling for one hour with 50 g. of sodium thiosulphate, adding 10 to 20 ml. of aniline in small portions (§ III, *e*, 1); the precipitate is collected on a loose paper, washed thoroughly with hot water, dried, and ignited. The residue is fused with bisulphate, the melt dissolved in 5 per cent. sulphuric acid, and the tervalent hydroxides are precipitated by cautious addition of ammonia and boiling until the liquid barely smells. The precipitate is collected, washed, and dissolved in hydrochloric acid; the solution is evaporated to a low volume, and the spark spectrum examined in the usual manner, employing a spark of about 2 mm. taken off the surface of the solution. Gallium gives an intense line in the violet at 4170A. and a distinct but much less intense line at 4031A.

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[1] L. M. Dennis and J. A. Bridgman, *J. Amer. Chem. Soc.*, 1918, **40**, 1552.

[2] W. Geilmann and F. W. Wrigge, *Zeitsch. anorg. Chem.*, 1932, **209**, 129.

[3] Authors' method. E. Reichel (*Zeitsch. anal. Chem.*, 1932, **87**, 321) recommends using an ammoniacal sulphate solution as electrolyte, but we prefer the procedure given *above.*

(*b*) *In Iron Ores.*—The ore is dissolved in hydrochloric acid or fused with bisulphate, the solution reduced with metallic zinc, and the gallium concentrated as described under (*a*).

(*c*) *In Bauxite.*—The ore is decomposed by fusion with potassium bisulphate, and the test continued as described under § VI, *c*.

§ **VI. Determination in Ores.**—(*a*) *In Zinc Ores and Iron Ores.*—Owing to the very minute amounts of gallium present in these ores, large amounts (*e.g.* 100 g.) must be taken for analysis. The gallium is concentrated into a small amount of precipitate by the procedure described in § V. The sulphate solution obtained by fusion of the ignited thiosulphate precipitate with bisulphate is neutralized with sodium hydroxide and poured into an excess of a solution of this reagent sufficient to give a 0·3N. alkali solution. The precipitate is filtered off, washed with hot 2 per cent. sodium nitrate solution, redissolved in nitric acid, and reprecipitated as before. The combined filtrates, containing all the gallia, are acidified with sulphuric acid and boiled with just sufficient ammonia to make the solution alkaline to cresol red; the precipitate is collected, washed six times with hot 2 per cent. sodium sulphate solution, and redissolved in sulphuric acid. The acidity is adjusted to 2N. and the gallium precipitated with cupferron (§ III, *d*), the precipitate being ignited to $Ga_2O_3$.

(*b*) *In Germanite.*—This mineral is the richest known source of gallium; it generally contains 0·7 to 0·8 per cent. For the analysis, 5 to 10 g. is dissolved in nitric acid and the solution evaporated with 20 ml. of sulphuric acid to expel the nitric acid. The residue is dissolved in 200 ml. of water, the solution boiled and filtered, the filtrate electrolysed to remove copper and arsenic, and the electrolyte (400 ml.) saturated with hydrogen sulphide to remove heavy metals, germanium, and molybdenum. The filtrate from the sulphides is neutralized with sodium carbonate and boiled with sodium thiosulphate and aniline as described *above*. The precipitate is treated as described under (*a*).

(*c*) *In Bauxite.*—The mineral (20 g.) is fused with bisulphate, and the melt leached with warm very dilute sulphuric acid. The solution is poured into an excess of sodium hydroxide solution sufficient to give a 0·3N. solution after all the aluminium and gallium are dissolved. The precipitate of ferric and titanium hydroxides is collected on a vacuum filter, washed with hot water, and redissolved in sulphuric acid. In case traces of gallia are entrained by the iron this solution is reduced with hydrogen sulphide and boiled with thiosulphate and aniline; the precipitated titania is collected, ignited and fused with bisulphate, and the sodium hydroxide treatment repeated. The combined alkaline solutions are acidified with hydrochloric acid. An excess of acid equal to one-quarter of the volume of solution is added, followed by 5 to 10 ml. of a 5 per cent. solution of potassium ferrocyanide, and after keeping at 60° to 70° C. for about an hour, the solution is set aside overnight. Any precipitate which forms is collected, washed, and tested for gallium as described in § III, *f*, the gallium being eventually recovered by the tannin method (§ III, *c*).

(*d*) *In Metallic Aluminium.*[1]—100 g. of metal is dissolved in hydrochloric acid and the solution evaporated to a thick syrup, which is stirred with 300 ml. of concentrated hydrochloric acid and 300 ml. of ether while cooling. Most of the aluminium separates as $AlCl_3.6H_2O$. The crystals are collected on a vacuum filter and washed with a 1 : 1 mixture of hydrochloric acid and ether. The filtrate is cautiously evaporated to a syrup and the process repeated with 200 ml. of the ether-hydrochloric acid mixture, saturating it cold with gaseous hydrogen chloride. It may be necessary to repeat the separation a third time using only 50 ml. of the acid-ether mixture. The final filtrate is evaporated to dryness and the gallium purified by precipitation with ammonium bisulphite, followed by solution in sodium hydroxide and precipitation with cupferron from sulphuric acid solution.

## X.—INDIUM.

§ **I. Minerals.**—Like gallium, indium is never found as the predominating metallic constituent of a mineral. *Cylindrite*, a complex sulphide of lead, antimony, and tin, may contain up to one per cent of indium.

The element occurs in traces in most zinc blendes, in tin ores, and in many samples of pyrites, siderite, and tungsten ores. Commercial zinc often contains small quantities of indium, which is recovered as a by-product in electrolytic zinc refining.

§ **II. Properties and Compounds.**—(*a*) The *metal* is soft, ductile, and silver-white, melts at 155° C., and volatilizes at a red heat. Sp. gr. 7·28. It burns in air at a red heat, and unites directly with sulphur and the halogens when heated. Neither boiling water nor aqueous caustic alkalis affect the metal, but it dissolves in mineral acids fairly readily. It may be precipitated from solutions of its salts by metallic zinc or by electrolysis.

(*b*) The *sesquioxide*, $In_2O_3$, is a yellow powder, soluble in acids if formed at a low temperature, but highly resistant if it has been ignited strongly. It is produced by ignition of indium salts of volatile acids, and is reduced to the metal when heated in hydrogen or ammonia, or with aluminium, carbon, or sodium. On heating above 850° C. it loses oxygen and is converted into $In_3O_4$.

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[1] After E. H. Swift, *J. Amer. Chem. Soc.*, 1924, **46**, 2375. See also I. Wada and S. Ato, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1922, **1**, 70.

(*c*) The *sulphide*, $In_2S_3$, is a yellow flocculent precipitate produced by hydrogen sulphide in a neutral or acetic-acid solution of the metal. It is soluble in strong mineral acids, also in a large excess of alkali sulphide. Potassium sulphide produces in indium solutions a white precipitate of hydrous potassium thioindate, $K_2In_2S_4.xH_2O$, soluble in excess. Lower sulphides may be prepared in the dry way.

(*d*) The *chlorides*.—Three are known: InCl, dark red; $InCl_2$, white crystals; and $InCl_3$, lustrous white tablets. The first two are decomposed by water with the formation of a solution of the third compound and deposition of the metal. The trichloride is a very deliquescent stable compound, only slightly hydrolysed in aqueous solution. It forms double compounds with chlorides of the alkali metals of the types $M_3InCl_6.2H_2O$ and $M_2InCl_5.H_2O$.

(*e*) The *sulphate*, $In_2(SO_4)_3$, is a very soluble compound formed by dissolving the metal or its oxide in sulphuric acid. It forms alums with cæsium, rubidium, and ammonium sulphates.

(*f*) The *basic sulphite*, $In_2(SO_3)_3.2In(OH)_3.5H_2O$, is precipitated by boiling the solution of an indium salt with excess of alkali bisulphite.

§ **III. Quantitative Separation.**—Indium, like gallium, follows aluminium in the ordinary course of analysis; its hydroxide is, however, insoluble in sodium hydroxide solution. Indium is not precipitated by hydrogen sulphide from solutions of its salts containing a strong mineral acid, but in acetic acid or very dilute hydrochloric acid solution (0·05N.) hydrogen sulphide gives a precipitate of yellow indium sulphide; in ammoniacal solutions a white precipitate is produced by addition of ammonium sulphide, and both precipitates are slightly soluble in hot yellow ammonium sulphide. Barium carbonate, hexamethylenetetramine, and potassium cyanate precipitate indium hydroxide from nearly neutral solutions, even in the presence of ammonium salts (distinction from zinc, etc.), while boiling with ammonium bisulphite precipitates a basic indium sulphite. Indium is precipitated from solutions of its salts by treatment with metallic zinc; this procedure serves to separate the metal from gallium, aluminium, zirconium, etc., which are not reduced.

(*a*) *From Metals of the Hydrogen-sulphide Group.*—Although indium is not precipitated by hydrogen sulphide from acid solutions, if other precipitable metals are present their sulphides are liable to be contaminated with indium; hydrogen sulphide is, therefore, best avoided as a means of separating the heavy metals.

(1) *From tin, antimony, and bismuth.* The nitrate solution is evaporated to dryness and the residue heated at 120° C., cooled, and extracted with 5 per cent. ammonium nitrate solution; the insoluble compounds of the above metals are filtered off, and the indium is recovered from the filtrate by addition of ammonia.

(2) *From arsenic.* The solution is evaporated to dryness with hydrochloric acid and 1 g. of potassium iodide, the residue moistened with hydrochloric acid and again dried, and the process repeated once more to ensure complete volatilization of the arsenic.

(3) *From lead.* Evaporation of solutions containing both lead and

indium with sulphuric acid until fumes of the acid are evolved leads to serious contamination of the lead sulphate with indium. No satisfactory separation of these two metals appears to be given in the literature, but we have obtained good results by precipitation of most of the lead from a feebly acid nitrate solution of the two metals by addition of 2 g. of ammonium sulphate, followed by neutralization of the filtrate with ammonia (avoiding a permanent precipitate), addition of 10 g. of ammonium acetate, and precipitation of the indium by boiling with 0·5 to 1 g. of hexamethylenetetramine. The last traces of lead may be recovered from the indium filtrate by treatment with hydrogen sulphide.

(*b*) *From Cadmium, Zinc, Copper, Nickel, Cobalt, and Manganese.*—The solution is treated with 5 g. of ammonium nitrate and boiled with the cautious addition of ammonia until just alkaline to methyl red; the precipitate of indium hydroxide is collected, washed with hot water containing 1 per cent. of ammonium nitrate, redissolved in nitric acid, and reprecipitated as before.

(*c*) *From Cadmium, Zinc, Copper, Nickel, and Cobalt.*[1]—The chloride solution is neutralized with ammonia and treated with potassium cyanide sufficient to redissolve the cyanides of these elements and to decolorize the solution; 5 ml. of 10 per cent. potassium cyanate solution is then added and the mixture boiled under a hood until the indium hydroxide flocculates. Reprecipitation is necessary if the amount of other metals present exceeds ten times that of the indium.

(*d*) *From Manganese, Aluminium, and Iron.*[1]—The chloride solution is neutralized with ammonia, avoiding a permanent precipitate, diluted to 200 ml., acidified with 5 ml. of N. hydrochloric acid, saturated cold with hydrogen sulphide, and finally heated at 70° C. for two hours while the gas is still passing. The precipitated indium sulphide is collected with the aid of a little filter-pulp, washed with hydrogen-sulphide water, and redissolved in hydrochloric acid; after boiling off the hydrogen sulphide the solution is cooled, neutralized, and adjusted to 0·025N. hydrochloric acid as before; the indium is again precipitated with hydrogen sulphide in the same way. The combined filtrates should be tested for complete precipitation by cautious addition of very dilute ammonia until a small black precipitate (ferrous sulphide) is obtained; this is collected, washed, redissolved in hydrochloric acid, and the solution tested for indium as *above*.

(*e*) *From Gallium.*—This is best accomplished by precipitation of indium with strip zinc from a very slightly acid cold chloride solution, care being taken to leave the solution distinctly acid, otherwise basic gallium salts may be precipitated.

§ **IV. Gravimetric Determination.**—(*a*) *As Indium Sesquioxide.*—Indium is usually weighed as the oxide $In_2O_3$ obtained by cautious ignition of the hydroxide produced by boiling the nitrate solution with ammonium nitrate and ammonia in very slight excess. If the solution contains chlorides these must be rigorously removed by thorough washing of the precipitate with 2 per cent. ammonium nitrate solution; reprecipitation may be advisable if much chloride is present, since indium chloride is very volatile. Indium oxide is readily reduced to metal, so the precipitate and paper must be charred at a low temperature and the carbon burned away at below 800° C.; the oxide should not be ignited above 800° C., since it is partially reduced to $In_3O_4$ at 850° C.

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[1] L. Moser and F. Siegmann, *Monatsh.*, 1930, **55**, 14.

(*b*) *As the* 8-*Hydroxyquinoline Compound*.[1]—The neutral chloride solution is treated with 2 g. of sodium acetate and 2 ml. of glacial acetic acid, diluted to 100 ml., heated to 70° to 80° C., and treated with a 5 per cent. solution of 8-hydroxyquinoline in 30 per cent. acetic acid until no further precipitate forms. The warm solution is filtered through a sintered glass crucible under gentle suction, and the precipitate washed with warm water, dried at 105° to 120° C. for one hour, and weighed as $(C_9H_6ON)_3In$, which contains 20·97 per cent. of indium.

(*c*) *By Electrolysis.*—The sulphate solution is neutralized with ammonia, avoiding a permanent precipitate, treated with 10 g. of ammonium sulphate, and electrolysed cold with 0·2 amp. between a platinum gauze cathode and a platinum spiral anode. Next morning the cathode is removed without breaking the current, washed with cold water, then with alcohol, dried, and weighed. More rapid deposition is obtained by gently rotating the cathode during electrolysis.

(*d*) *As Sulphide*, $In_2S_3$.—L. Moser and F. Siegmann[2] state that the sulphide obtained by precipitation with hydrogen sulphide as described in § III, *d*, or from a feebly acid acetate solution, can be weighed after heating at 350° to 400° C. in a current of hydrogen sulphide, but we prefer to use one of the preceding methods, which are much more convenient.

§ **V. Detection in Ores.**—The solution of the ore in a suitable acid (hydrochloric acid for iron or zinc ores, or *aqua regia* for pyrites) is treated with strip zinc to precipitate indium with the heavy metals, the precipitate is dissolved in nitric acid, bismuth, tin, and antimony are removed as described in § III, *a*, 1, and the filtrate is treated with ammonia to obtain an indium concentrate. The ammonia precipitate is dissolved in hydrochloric acid, the solution evaporated to dryness, the residue dissolved in water, and the solution boiled with 1 g. of sodium bisulphite. If any precipitate forms it is collected, washed, and dissolved in hydrochloric acid; the solution is then examined spectroscopically by the flame method on a small coil of platinum wire. Indium colours the flame bluish-violet and gives two very characteristic lines, one in the blue at 4511·5A. and the other in the violet at 4102A.

§ **VI. Determination in Ores.**—Since only very small quantities of indium are found in any ore, at least 100 g. must be taken for analysis. Iron ores and zinc ores are decomposed as described under gallium (**IX**), and the indium is concentrated by precipitation on strips of metallic zinc, the resulting sponge being dissolved in nitric acid and the solution evaporated to dryness to remove bismuth, etc.

Tin ores are best reduced in hydrogen or by fusion with potassium cyanide to give a button of metallic tin, which is granulated and dissolved in nitric acid; the resulting metastannic acid is filtered off, the filtrate is evaporated to dryness, the residue moistened with hydrochloric acid and dried again, and the resulting chloride solution precipitated with zinc, etc., as described *above*.

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[1] W. Geilmann and F. W. Wrigge, *Zeitsch. anorg. Chem.*, 1932, **209**, 129.

[2] *Monatsh.*, 1930, **55**, 17.

The nearly neutral nitrate solution obtained by either of the above methods is treated with 5 g. of ammonium nitrate and a little filter-pulp and boiled with the cautious addition of a 2 per cent. solution of hexamethylenetetramine until no further flocculent precipitate forms. The precipitate is collected on a loose filter, washed with 2 per cent. ammonium nitrate solution, dissolved in nitric acid and reprecipitated as before, after neutralization of the solution with ammonia. The second precipitate is washed with 2 per cent. ammonium sulphate solution and dissolved in 5 per cent. sulphuric acid; the solution, filtered if necessary, is neutralized with sodium carbonate, avoiding a permanent precipitate, and the indium precipitated as basic sulphite by boiling with 5 g. of sodium bisulphite until all sulphur dioxide is expelled. The precipitate is collected, washed with cold water, and dissolved in dilute sulphuric acid; the solution is neutralized with ammonia, and the indium finally precipitated as hydroxide by boiling with hexamethylenetetramine. The precipitate is washed with 2 per cent. ammonium nitrate solution and ignited to $In_2O_3$ (§ IV, *a*).

## XI.—THALLIUM.

§ **I. Minerals.**—(*a*) *Crookesite*, a selenide, $(Cu,Tl,Ag)_2Se$, is an amorphous, brittle, lead-grey mineral with metallic lustre. H. 3; sp. gr. 6·9.

(*b*) *Lorandite*, thallous thioarsenite, $TlAsS_2$, is a deep red, translucent, monoclinic mineral possessing a metallic to adamantine lustre. It is usually found in modified tablets, which have a perfect basal cleavage. Streak dark red. H. 2½; sp. gr. 5·5.

(*c*) *Hutchisonite* consists of the sulphides of thallium, silver, copper, lead, and arsenic. Colour and streak vermilion. Transparent to translucent, brittle, orthorhombic, flat prisms, with adamantine lustre and good cleavage. H. 1½; sp. gr. 4·6.

(*d*) *Vrbaite*, $TlAs_2SbS_5$, occurs in deep red, translucent, orthorhombic crystals.

(*e*) In addition to the above, thallium is also found in very small quantities in rocks and minerals associated with the alkali metals, zinc, lead, iron, etc.; *e.g.* in sylvine, carnallite, lepidolite, alunite, zinc blende, pyrites, hæmatite, braunite, etc.; it tends to concentrate in some of the products when these minerals are worked up. Thus, small amounts of the element are sometimes met with in zinc, cadmium, platinum, bismuth, tellurium, etc., and in chamber mud and flue-dust from sulphuric acid plants.

§ **II. Properties and Compounds.**—(*a*) The *metal* is soft, of a bluish-white colour, and easily cut by a knife, the exposed surface exhibiting a bright metallic lustre, which soon tarnishes. It exists in two enantiotropic modifications, melts at 302° C., and has a sp. gr. of 11·85. A bar of the metal gives a "cry," like tin, when bent. It readily dissolves in sulphuric or nitric but only slowly in hydrochloric acid, and combines with oxygen slowly at ordinary temperatures, rapidly at 100° C.

(*b*) *Thallous oxide*, $Tl_2O$, is a heavy, black powder formed by oxidation of the metal in warm air or oxygen, or by dehydration of the corresponding hydroxide at 100° C. It readily absorbs moisture from the air, melts at 300° C., and, when fused, attacks glass.

(*c*) *Thallous hydroxide*, $TlOH$, crystallizes in yellow needles readily soluble in water, giving a colourless, strongly alkaline solution, which readily absorbs carbon dioxide, and attacks glass and porcelain. It is produced by the action of baryta on the sulphate.

(*d*) *Thallic oxide*, $Tl_2O_3$, a black powder formed by oxidation of the metal between 600° and 700° C., or small black crystals obtained by heating thallous nitrate to 450° C.; melts at 725° C., decomposes above 800° C., and is insoluble in water, alkalis, or cold sulphuric acid. With hot sulphuric acid it gives thallous sulphate and oxygen; with hydrochloric acid, chlorine and thallous and thallic chlorides.

(*e*) *Thallic hydroxide*, $TlO.OH$, is a brown powder, produced by the action of a slight excess of alkali on solutions of thallic salts. It is insoluble in water.

(*f*) *Thallous chloride*, $TlCl$, crystallizes as white cubes from a solution of thallous salt to which a soluble chloride has been added. One part dissolves in 400 parts of cold and 40 of hot water.

(*g*) *Thallous chloroplatinate*, $Tl_2PtCl_6$, is a pale yellow crystalline precipitate, soluble in 15,585 parts of cold and 1948 of boiling water. At a red heat it gives a thallium-platinum alloy.

(*h*) *Thallous iodide*, $TlI$, is precipitated as citron-yellow, orthorhombic crystals when a soluble iodide is added to a solution of a thallous salt. If heated to 168° C. it becomes red and cubic; the freshly precipitated compound turns green on exposure to the light. 100 parts of water dissolve 0·006 part of the salt at 20° and 0·12 at 100° C.

(*i*) *Thallous sulphide*, $Tl_2S$, is thrown down on passing hydrogen sulphide through a neutral, alkaline, or acetic-acid solution of a thallous salt as a black precipitate insoluble in alkali cyanide, sulphide, or hydroxide, or in acetic acid. It forms definite compounds with tin and arsenic sulphides, *e.g.* $Tl_4SnS_4$ and $Tl_3AsS_4$, which may be used for its gravimetric estimation.

(*j*) *Thallous sulphate*, $Tl_2SO_4$, is soluble in 20 parts of cold and 5 of hot water. It crystallizes in anhydrous rhombic prisms isomorphous with potassium sulphate, and may be fused without decomposition.

(*k*) *Thallous nitrate*, $TlNO_3$, is isodimorphous with potassium nitrate.

(*l*) *Thallic halides*, *sulphate* and *nitrate* are soluble in water, but readily hydrolyse, giving brown basic salts or thallic hydroxide. They readily combine with thallous salts, giving rise to many series of thallo-thallic compounds.

§ **III. Quantitative Separation.**—Thallous salts behave like those of lead in giving sparingly soluble precipitates in the cold with hydrochloric acid, potassium iodide, and potassium chromate. The sulphide can be precipitated only from alkaline solutions and is readily soluble in dilute acids, but under certain conditions thallium is coprecipitated with tin or arsenic sulphide as thallous thiostannate or thioarsenate. Thallous salts resemble those of potassium in giving no precipitate with ammonia or sodium carbonate, but crystalline precipitates with chloroplatinic acid and sodium cobaltinitrite. Thallic salts give with ammonia a brown precipitate resembling ferric hydroxide. Thallous salts are oxidized to thallic by chlorine or *aqua regia*, but not by nitric acid alone.

Precipitation with potassium iodide as a means of separating thallium from other metals, and the determination of thallium as iodide, have been condemned by L. Moser and A. Brukl,[1] who recommend using potassium chromate as the precipitant, a process first proposed by P. E. Browning and G. P. Hutchins.[2] The following separation procedures are due to Moser and Brukl, who have shown that methods depending on the precipitation of the common metals with sodium carbonate, the sulphate method of separating lead, and the iodide method of separating copper are quite unreliable. In all the separations described the thallium must be present in the univalent form; if thallic salts are present, sulphur dioxide should be added and the excess boiled off before making a separation.

(*a*) *From Arsenic and Antimony.*—The solution is treated with ammonia and boiled with 1 to 2 ml. of 6 per cent. hydrogen peroxide to convert the arsenic and antimony into the quinquevalent form; thallium is then precipitated as chromate.

(*b*) *From Tin.*—The solution is neutralized with ammonia, re-acidified with acetic acid, diluted to 500 ml., and boiled with 2 to 3 g. of ammonium nitrate to precipitate the tin as metastannic acid. The filtrate is evaporated to a low volume (50 to 80 ml.), made just ammoniacal, and treated with potassium chromate to precipitate the thallium.

(*c*) *From Lead, Bismuth, and Manganese.*—The nitrate solution is heated to boiling, and sufficient diammonium phosphate added to precipitate the bismuth as crystalline $BiPO_4$, which is collected and washed with hot water. The filtrate is treated with 20 ml. of 30 per cent. sulphosalicylic acid solution, more diammonium phosphate, and sufficient ammonia to precipitate completely the lead and manganese. The thallium in the filtrate is then recovered as in (*b*).

(*d*) *From Silver, Mercury, and Copper.*—The solution is made ammoniacal and treated with potassium cyanide to convert these metals into soluble double cyanides; the thallium is then precipitated as chromate.

(*e*) *From Gallium, Indium, Aluminium, Iron, Chromium, Zinc, Cadmium, Nickel, Cobalt, and Selenium.*—The solution is treated with 20 ml. of 30 per cent. sulphosalicylic acid solution, ammonia until alkaline, and potassium chromate to precipitate the thallium. In the absence of the first five metals in the above list, addition of sulphosalicylic acid is unnecessary, sufficient ammonia and ammonium nitrate being added to keep the bivalent metals in solution.

(*f*) *General Separation Procedure.*—Thallium may be separated as chromate from an unknown solution which may contain any of the above metals by the following combined procedure: The acid nitrate solution is treated with 20 to 30 ml. of 30 per cent. sulphosalicylic acid, then with an excess of ammonium phosphate, made ammoniacal, and boiled. Any precipitate is filtered off and washed with hot 2 per cent. ammonium nitrate solution; the filtrate is evaporated to 80 to 100 ml., cooled, and treated with potassium cyanide until colourless, and the thallium precipitated by potassium chromate.

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[1] *Monatsh.*, 1926, **47**, 709.

[2] *Amer. J. Sci.* (4), 1899, **8**, 460.

§ **IV. Gravimetric Determination.**—(*a*) *As Chromate.*—The solution (containing the whole of the thallium in the univalent form, and of a total volume of not more than 100 ml.) is rendered distinctly ammoniacal, heated to boiling, and treated with stirring with sufficient potassium chromate to give a 2 per cent. solution after precipitation of the thallium is complete. After standing overnight in a cool place, the precipitate is collected in a sintered glass crucible, washed with cold 1 per cent. potassium chromate solution, then with 50 per cent. alcohol, dried at 120° C., and weighed as $Tl_2CrO_4$, which contains 77·89 per cent. Tl.

The solubility of thallous chromate in mg. per litre is as follows: water, 42·7; 60 per cent. alcohol, 9·2; 2 per cent. ammonia + 2 per cent. potassium chromate, 9·5; 5 per cent. ammonia + 2 per cent. potassium chromate, 14·2. Hence precipitation should be made in only feebly ammoniacal solutions, and the minimum amount of wash water used.

(*b*) *As Cobaltinitrite.*[1]—The nearly neutral thallous solution is treated at 80° C. with an excess of sodium cobaltinitrite solution, whereby a brick-red precipitate of $NaTl_2Co(NO_2)_6$ is thrown down. After cooling the precipitate is collected in a sintered glass crucible, washed with cold water, dried at 110° C., and weighed; it contains 53·31 per cent. Tl.

The reagent is prepared by mixing equal volumes of solutions containing (i) 57·2 g. of cobalt nitrate crystals and 100 ml. of acetic acid per litre, and (ii) 360 g. of sodium nitrite per litre. The mixture, which does not keep well, is made 12 hours in advance and filtered immediately prior to use.

(*c*) *As Metal.*—The slightly acid chloride or sulphate solution is boiled with pure magnesium turnings in a flask fitted with a Bunsen valve. When effervescence ceases the solution is cooled, ammonium chloride added, and the mixture shaken until all the magnesium has dissolved. The solution is decanted carefully from the heavy precipitate of thallium sponge, a weighed quantity of Wood's metal is added, and the whole gently warmed until the latter melts and collects the thallium. After cooling, the metal button is washed with cold water, dried, and weighed; the increase in weight represents thallium. This procedure is simple and sufficiently accurate for medium to large quantities of thallium, and can be applied when the original solution contains any metal not precipitated by magnesium.

(*d*) *As the Thionalide Compound.*—R. Berg and E. S. Fahrenkamp[2] state that thioglycollic β-naphthylamide (thionalide) is a specific reagent for thallium and can be used for its gravimetric determination. For this purpose they proceed as follows:

The slightly acid solution (100 ml.) is treated in succession with 10 to 25 ml. of 20 per cent. sodium tartrate solution, 2N. sodium hydroxide solution until just alkaline to phenolphthalein, 20 per cent. potassium cyanide solution until the mixture contains 5 per cent. of cyanide, and more of the sodium hydroxide to make the solution 2N. in alkalinity, allowing or the alkali derived from the cyanide. The thallium is then precipitated by adding a solution of 0·4 to 0·5 g. of thionalide dissolved in 8 to 10 ml. of acetone for every 0·1 g. of thallium present; the mixture is boiled and cooled, and the precipitate of $C_{10}H_7.NH.CO.CH_2.STl$ collected in a glass filter-crucible, washed with cold water, then with acetone, dried at 100° C., and weighed; it contains 48·60 per cent. Tl. If mercury, bismuth, or lead is present in the original solution, more precipitant must be added followed by sufficient acetone to give at least 30 per cent. of acetone in the mixture, so as to keep the thionalide compounds of these metals in solution.

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[1] W. Strecker and P. de la Peña, *Zeitsch. anal. Chem.*, 1925, **67**, 256.

[2] *Zeitsch. anal. Chem.*, 1937, **109**, 305.

§ V. **Volumetric Determination.**—The volumetric methods for the determination of thallium are all based on the principle of oxidizing thallous salts to thallic; owing to the ease with which thallic salts are hydrolysed, however, simple titration of sulphate solutions with permanganate does not give satisfactory results. Hydrochloric-acid solutions are much more satisfactory, but permanganate is not the best oxidant owing to its action on the acid. All the numerous other oxidants which have been recommended in the literature appear to have some disadvantages, although potassium iodate [1] is stated to yield good results. In our opinion none of the volumetric methods is suitable for use in ore analysis.

§ **VI. Detection in Ores.**—The ore is dissolved in nitric acid, the solution evaporated to dryness with 2 to 3 drops of sulphuric acid, and the residue heated cautiously until no further brown fumes are evolved, then at a low red heat. The product is extracted with hot 2 per cent. sulphuric acid, the insoluble material filtered off, the filtrate boiled with a slight excess of sodium carbonate, and any precipitate removed by filtration. The alkaline filtrate is cooled, treated with a few ml. of potassium cyanide solution, and saturated with hydrogen sulphide. Any precipitate is collected, washed with cold water containing a little ammonium sulphide, and dissolved in dilute sulphuric acid. The following tests are applied:

(*a*) A platinum wire dipped in a mixture of a few drops of the solution with an equal volume of 1 : 1 hydrochloric acid, and held in a Bunsen flame, colours the latter green, and the spectroscope shows a characteristic green line at 5351A.

(*b*) Potassium iodide gives a yellow crystalline precipitate.

(*c*) Potassium chromate gives a yellow precipitate in the feebly ammoniacal solution.

(*d*) Treatment of the solution with zinc precipitates a metallic sponge, readily soluble by boiling with an excess of sulphuric acid.

§ **VII. Determination in Ores.** — (*a*) *Determination in Thallium Minerals.*—One g. of the finely powdered mineral is dissolved by gentle heating with 10 to 15 ml. of 1 : 1 nitric acid, the solution evaporated to dryness on the water-bath, and the residue extracted with 50 to 60 ml. of boiling water. After filtering off any insoluble material, the solution is treated as described in § III, *f* to precipitate the thallium as chromate, in which form it is weighed.

(*b*) *Determination in Pyrites, Blende, etc.*—From 10 to 100 g. of mineral is dissolved in hot hydrochloric acid (blende) or a 3 : 1 mixture of nitric and hydrochloric acids (pyrites); in the first case some nitric acid is added towards the end of the reaction to ensure complete attack of the sulphides. In either case the solution is evaporated to dryness and the nitric acid expelled by evaporation with sulphuric acid. The solution is then nearly neutralized with ammonia and treated exhaustively with strip zinc until no further precipitate forms. The metallic sponge is collected, washed several times with hot water, and boiled with 10 per cent. sulphuric acid until nothing further is extracted; the filtered solution is then treated as described in § III, *f*.

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[1] E. H. Swift and C. S. Garner, *J. Amer. Chem. Soc.*, 1936, **58**, 113.

## XII.—THE RARE-EARTH METALS.

§ **I. Minerals.**—(*a*) *Those in which the Cerium Group predominates.*—(1) *Carbonates.* (α) *Parisite*, a fluocarbonate of cerium metals and lime, $CaCe_2F_2(CO_3)_3$, occurs as brownish-yellow to red, acute double hexagonal pyramids with perfect cleavage and strong positive double refraction. H. 4½; sp. gr. 4·26.

(β) *Cordylite*, the barium analogue of the above, has similar properties.

(γ) *Bastnäsite*, cerium fluocarbonate, $CeFCO_3$, occurs as yellow to brown hexagonal prisms of H. 4; sp. gr. 5·0.

(δ) *Lanthanite*, hydrous carbonate of the cerium metals, chiefly lanthanum, $La_2(CO_3)_3.8H_2O$. White to yellowish, opaque, orthorhombic tables. Cleavage perfect. Usually found amorphous as an alteration product. H. 2; sp. gr. 2·6.

(2) *Silicates.* (α) *Cerite*, a hydrous silicate of cerium metals, lime, and ferrous oxide, is a brittle, opaque, brown to red, orthorhombic mineral, usually occurring massive. No cleavage, dull resinous lustre. H. 5½; sp. gr. 4·9.

(β) *Allanite* (*orthite*) is an epidote containing rare earths. Brown to black, opaque monoclinic crystals. H. 6; sp. gr. 3·5 to 4·2. On heating it becomes amorphous, and denser.

(γ) *Hellandite*, a complex hydrous silicate, $3H_2O.(Ca_2,Th,Mg_2)O_2.3(Al,Fe,Mn,Ce)_2O_3.4SiO_2$. Red-brown monoclinic prisms. H. 5¼; sp. gr. 3·7.

(δ) *Beckelite*, a zirconosilicate of cerium metals and calcium, $Ca_3Ce_4(Si,Zr)_3O_{15}$, is found in brown transparent octahedra and dodecahedra with cubic cleavage. Sp. gr. 4·1.

(3) *Miscellaneous.* (α) *Aeschynite.* See **XVIII,** § I, *b*, 1.

(β) *Monazite.* See **XV,** § I, *c*, 1.

(*b*) *Those in which Yttria Earths predominate.*—(1) *Silicates.* (α) *Gadolinite*, ferrous beryllium yttrium silicate, $2BeO.FeO.Y_2O_3.2SiO_2$; brown to greenish-black, brittle, massive; no cleavage, conchoidal fracture. H. 7; sp. gr. 4·0 to 4·5. Glows when heated to 430° C., and is then insoluble in acids, the amorphous variety becoming crystalline and denser.

(β) *Rowlandite*, yttrium silicate, $2Y_2O_3.3SiO_2$, pale green, massive, translucent. Sp. gr. 4·5.

(γ) *Yttrialite*, yttrium silicate, $Y_2O_3.2SiO_2$, massive, amorphous, translucent, olive-green. H. 5½; sp. gr. 4·6.

(δ) *Thalenite*, hydrous yttrium silicate, $H_2O.2Y_2O_3.4SiO_2$, contains much nitrogen and helium. Flesh-red, translucent, monoclinic tables with greasy lustre, no cleavage. H. 6½; sp. gr. 4·2.

(2) *Titanosilicates and Titanates.* (α) *Yttrotitanite* or *keilhauite*, a complex titanosilicate of iron, lime, alumina, and yttria. Brown to black, monoclinic. Streak grey-brown, distinct cleavage, resinous lustre. H. 6½; sp. gr. 3·6.

(β) *Yttrocrasite*, a complex titanate of yttrium, with calcium, thorium, uranium, lead, iron. Radioactive, black, with bright pitchy lustre. H. 5½; sp. gr. 4·8.

(γ) *Delorenzite*, ferrous uranium yttrium titanate, $2FeO.UO_2.2Y_2O_3.24TiO_2$, resinous, black, orthorhombic crystals; radioactive. H. 5·5; sp. gr. 4·7.

(3) *Miscellaneous.* (α) *Xenotime*, yttrium phosphate, $YPO_4$, brown to red-brown or yellow, transparent to opaque. Tetragonal; cleavage perfect. H. 4½; sp. gr. 4·5.

(β) *Yttrofluorite*, yttrium calcium fluoride, $2YF_3.3CaF_2$, yellow to brown, transparent cubes, with poor octahedral cleavage. Vitreous to greasy lustre, brittle. H. 4½; sp. gr. 3·6.

(γ) *Yttrocerite*, yttrium cerium calcium fluoride, $(Y,Ce)_2Ca_3F_{12}.2/3H_2O$; violet-blue to white, massive; vitreous to pearly lustre. H. 4½; sp. gr. 3·4.

(δ) *Samarskite*, *fergusonite*, *euxenite*, etc. See **XVIII**, § I.

§ **II. Properties and Compounds.**—The "Rare-earth Metals" comprise a series of some sixteen very closely allied metals, which are usually found together in Nature and are extremely difficult to separate from one another. They may, however, be separated roughly into three groups by a method based on differences in the solubilities of their double sodium sulphates in a cold saturated solution of sodium sulphate:

| *Cerium Group:* Insoluble Double Sulphates. | | | *Terbium Group:* Sparingly Soluble Double Sulphates. | | | *Yttrium Group:* Soluble Double Sulphates. | | |
|---|---|---|---|---|---|---|---|---|
| Element. | At. No. | At. Wt. | Element. | At. No. | At. Wt. | Element. | At. No. | At. Wt. |
| Lanthanum (La) . | 57 | 138·92 | Europium (Eu) . | 63 | 152·0 | Yttrium (Y) . | 39 | 88·92 |
| Cerium (Ce) . | 58 | 140·13 | Gadolinium (Gd) | 64 | 156·9 | Dysprosium (Dy) | 66 | 162·46 |
| Praseodymium (Pr) | 59 | 140·92 | Terbium (Tb) . | 65 | 159·2 | Holmium (Ho) . | 67 | 163·5 |
| Neodyium (Nd) . | 60 | 144·27 | | | | Erbium (Er) . | 68 | 167·2 |
| ?Illinium (Il) . | 61 | . . | | | | Thulium (Tm) . | 69 | 169·4 |
| Samarium (Sm) . | 62 | 150·43 | | | | Ytterbium (Yb) . | 70 | 173·04 |
| | | | | | | Lutecium (Lu) . | 71 | 175·0 |

No pure compounds of illinium have yet been prepared; indications of its existence have, however, been obtained by spectrographic and X-ray analysis.

In analysis no sharp separation of the metals into these three groups can be made, since the solubilities of the double sulphates show a slow gradation with increasing atomic number; generally the terbium group divides itself between the cerium and yttrium groups when sodium sulphate is used as precipitant, and mostly follows the cerium group when the potassium salt is used.

In their stable salts the metals are all tervalent, but samarium, europium, and ytterbium form unstable salts in which they are bivalent, and cerium unstable salts in which it is quadrivalent. Cerium, praseodymium, and terbium form stable dioxides; the other metals form stable sesquioxides only. The trihydroxides of the metals are strong bases, the strength of which decreases with increasing atomic number; yttrium hydroxide occupies, however, an anomalous position, being not quite so strong a base as lanthanum hydroxide. The more strongly basic oxides liberate ammonia from ammonium salts and absorb carbon dioxide from the air. From the analyst's point of view the most characteristic property of the rare-earth metals is the insolubility of their oxalates in dilute mineral acids; this fact is utilized in separating the metals from all other metals except thorium and scandium.

(*a*) The *metals* can be prepared by electrolysis of the fused anhydrous chlorides or by reduction of these salts with metallic potassium *in vacuo*. They are brittle and vary in colour from yellowish to dark grey; all have a high affinity for oxygen and rapidly oxidize in contact with moist air. The melting-points of the metals are: cerium 630°, lanthanum 812°, praseodymium 932°, neodymium 840°, and samarium 1350° C.; their specific gravities are 6·8, 6·15, 6·47, 7·0, and 7·7 respectively. Hardly any definite data are available for the yttrium and terbium groups of metals.

(*b*) The *sesquioxides* are fairly strong bases, which are readily soluble in dilute acids after ignition. They may be prepared by ignition of the oxalates, nitrates, or hydroxides; cerium sesquioxide, however, oxidizes to the dioxide in air, while praseodymia and terbia are formed only after ignition of their salts in hydrogen.

(1) *Ceria*, $CeO_2$, obtained by ignition of cerous oxalate is a dense pale yellow powder, but ignition of the basic sulphate yields a less dense white oxide which has been proposed as a substitute for tin oxide for opacifying enamels. The oxide is insoluble in acids except hot concentrated sulphuric acid, in which it dissolves slowly giving orange-red ceric sulphate, which on further heating decomposes into white cerous sulphate.

(2) *Lanthana*, $La_2O_3$, is a white powder which readily absorbs carbon dioxide from the air, and hisses like lime when slaked.

(3) *Praseodymia*, $Pr_2O_3$, is a greenish-yellow powder which oxidizes to oxides intermediate between $Pr_2O_3$ and $PrO_2$ when heated in the air. Ignition of the oxalate in the air affords a brown oxide approximating to $Pr_4O_7$, while the black dioxide is obtained pure by anodic oxidation of a solution of the sesquioxide in fused sodium hydroxide, or by decomposition of the nitrate at 400° C.

(4) *Neodymia*, $Nd_2O_3$, is a pale lilac-blue powder when pure, but traces of other earths turn it brownish.

(5) *Samaria*, $Sm_2O_3$, is a heavy yellowish-white powder.

(6) *Yttria*, $Y_2O_3$, is a white powder resembling lanthana.

(7) *Dysprosia*, $Dy_2O_3$, is white; *holmia*, $Ho_2O_3$, pale yellow; *erbia*, $Er_2O_3$, pale rose; *thulia*, $Tm_2O_3$, white with a greenish tinge; *ytterbia*, $Yb_2O_3$, white; and *lutecia*, $Lu_2O_3$, white.

(*c*) *Salts.*—The salts of tervalent cerium, lanthanum, yttrium, ytterbium, and lutecium are colourless, those of praseodymium and thulium green, those of neodymium deep lilac-rose with a bluish fluorescence, those of erbium rose-pink, and those of samarium, dysprosium, and holmium pale yellow.

(1) The *chlorides* are very soluble; except for the praseodymium salt, which forms a heptahydrate, they crystallize with six molecules of water.

(2) The *fluorides* are insoluble in water and dilute mineral acids, but slightly soluble in concentrated hydrochloric acid. Hydrous salts are precipitated by addition of a soluble fluoride to rare-earth chloride solutions.

(3) The *sulphates* are readily soluble in ice-cold water, but on heating the solution deposits hydrous salts. Lanthanum sulphate crystallizes as the hexagonal enneahydrate at 25° C., while the other sulphates crystallize as monoclinic octahydrates. All the sulphates readily form double sulphates with the alkali sulphates, those of the cerium group being insoluble and those of the yttrium group soluble in a saturated solution of the alkali sulphate.

(4) The *nitrates* are extremely soluble salts, those of the cerium and terbium groups forming readily crystallizable salts with the nitrates of the alkalis, magnesium, zinc, nickel, cobalt, and manganese; these double salts are, in some cases, isomorphous with the corresponding bismuth salts, a fact which is utilized in the separation of the earths by fractional crystallization.

*Ceric nitrate* forms an unstable orange solution which turns red on addition of ammonium nitrate. From this solution large, deep orange-red crystals of $(NH_4)_2Ce(NO_3)_6$ separate on evaporation; the crystals are only sparingly soluble in nitric acid.

(5) The *oxalates* are precipitated as decahydrates on addition of oxalic acid to solutions of the salts; the precipitates are amorphous at first, but become crystalline, more readily when the suspension is warmed and stirred. They are almost insoluble in water, the lanthanum salt being relatively the most soluble oxalate of the cerium group; the oxalates of the yttrium group, however, are slightly more soluble. The precipitates are very slightly soluble in dilute mineral acids, but the presence of free oxalic acid counteracts this solvent effect. The oxalates of the yttrium group are perceptibly soluble in ammonium oxalate solution.

(*d*) The *hydroxides* are obtained by the action of caustic alkali upon solutions of the salts as flocculent precipitates insoluble in excess of the precipitant. *Cerous hydroxide* is a powerful reducing agent; it gradually turns violet in the air, being finally oxidized to yellow *ceric hydroxide*. This is soluble in nitric acid, forming an orange solution; with hydrochloric acid it yields cerous chloride, chlorine being liberated.

§ **III. Quantitative Separation.**—The rare-earth metals are members of the third analytical group, their hydroxides being precipitated by ammonia in the presence of ammonium salt; complete precipitation, especially of the most strongly basic metals, however, is obtained only in the cold and with a large excess of ammonia. Precipitation with oxalic acid in acid solution serves to separate the rare earths from the other members of the third group.

(*a*) *From Metals of the Ammonia Group and from Phosphoric Acid.*—The chloride or sulphate solution containing not more than 1·5 g. of oxides and not more than 5 ml. of acid per 100 ml. is treated cold with an equal volume of a cold saturated solution of oxalic acid, added all at once without stirring. A white flocculent precipitate forms in clots immediately, but after ½ to 1 hour this falls into a crystalline powder; the solution is then stirred vigorously and set aside overnight (if stirred immediately after addition of oxalic acid the clots tend to harden when the precipitate is large, and the resulting lumps occlude considerable mother-liquor, which cannot be effectively removed in the subsequent washing). Next morning the precipitate is collected and washed thoroughly with 2 per cent. oxalic acid solution containing a few drops of nitric acid. If the original solution contained much phosphoric acid or foreign metals it is advisable to repeat the precipitation, either after igniting the oxalates to oxides and dissolving these in hydrochloric acid, or after converting the oxalates into hydroxides by digestion with hot 10 per cent. sodium hydroxide solution and dissolving these, after thorough washing with hot water, in the same acid.

(*b*) *From Thorium.*—This may be effected by any of the following methods (for details of which see **XV,** § III):

(1) By precipitation of the thorium from the neutral solution of the nitrates with hydrogen peroxide.

(2) By precipitation of the thorium from the neutral chloride solution with sodium thiosulphate (scandium is also completely precipitated by this method).

(3) By precipitation of the thorium in nitric-acid solution with potassium iodate.

(4) By precipitation of the thorium in neutral chloride solution with hexamethylenetetramine in the presence of ammonium chloride.

(*c*) *From Scandium.*—See **VIII,** § III.

(*d*) *Separation of the Rare Earths from One Another.*—Quantitative methods of separation are known only for cerium and, when more than a few per cent. is present (which is rarely the case), europium and ytterbium. An approximate separation into two groups can, however, be obtained by saturating the solution with sodium or potassium sulphate, which throws down the double alkali sulphates of the ceria group metals—cerium, lanthanum, praseodymium, neodymium, and samarium—and leaves a solution of the single sulphates of the yttria group. Traces of neodymium and samarium fail to precipitate, while traces of some of the yttria group pass into the precipitate. The terbia group is divided between the precipitate and filtrate, but in all minerals of commercial importance the amounts of these metals present are very small. An approximate separation of lanthanum from the other members of the ceria group can also be made if the ceria is separated first, and recently an approximate separation of praseodymium from neodymium has been described, as well as a method of separating relatively pure samarium from the ceria earths; since the latter process involves reduction in absolute alcoholic solution with the strict exclusion of air it will not be described here.[1]

(1) *Approximate separation of the cerium from the yttrium group.* (*a*) *The metals are in solution as chlorides or nitrates.* The solution is evaporated to dryness on the water-bath to expel free acid, the residue dissolved in the

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[1] For details see A. Brukl, *Angew. Chem.*, 1939, **52**, 151.

minimum of cold water to give a clear solution, and the solution treated with 250 ml. of a cold saturated solution of potassium sulphate followed by 5 g. of the solid salt. The mixture is vigorously stirred for some time, set aside overnight, and filtered next day; the precipitate is well washed with a cold saturated solution of potassium sulphate, rinsed back into the beaker and digested with boiling 10 per cent. sodium hydroxide solution, and the resulting hydroxides are collected on the same paper, thoroughly washed with hot water until free from sulphates, and redissolved in a minimum of hydrochloric acid. The chloride solution is evaporated to dryness and the whole procedure repeated; the hydroxides obtained in this step are dissolved in nitric acid, and the solution (100 ml.) is treated with an equal volume of a cold saturated solution of oxalic acid, which precipitates the oxalates of the cerium-group earths. The combined filtrates from the double sulphates are boiled with sodium hydroxide, the precipitate is collected, washed free from sulphate with hot water and dissolved in nitric acid, and the yttria earths are precipitated from this solution by addition of oxalic acid. The greater part of the terbia group metals follow the ceria earths in this separation, but if sodium sulphate is used as the precipitant most of the terbia group earths pass into the filtrate with the yttria group.

($\beta$) *The metals are present as sulphates.* The solution is slowly poured into an excess of boiling 10 per cent. sodium hydroxide solution with vigorous stirring, the precipitate collected, washed free from sulphates with hot water, and dissolved in hydrochloric acid, and the solution treated as described under ($\alpha$) *above.*

($\gamma$) *Sulphamic acid method.*[1] The earths are precipitated as hydroxides as described under ($\beta$), and the precipitate is dissolved in sulphamic acid; the cooled solution is treated with solid sodium nitrite, which precipitates the double sulphates of the cerium earths, thus:

$$2M(SO_3NH_2)_3 + 6NaNO_2 = M_2(SO_4)_3 + 3Na_2SO_4 + 6N_2 + 6H_2O.$$

(2) *Separation of cerium from the other rare earths.* This separation depends on the fact that cerous nitrate is easily oxidized in solution to ceric nitrate, which is readily hydrolysed with the precipitation of basic salts, and which also yields an iodate insoluble in nitric acid solutions. All the other earths remain in the tervalent form, in which they yield soluble iodates.

($\alpha$) *Iodate method.*[2] The nitrate solution, which should contain not more than about 0·15 g. of ceria, is adjusted by dilution or evaporation to 50 ml., and treated with 25 ml. of nitric acid (sp. gr. 1·4) and 0·5 g. of potassium bromate; when this has dissolved, the ceria is precipitated by the slow addition, with vigorous stirring, of 50 ml. of a 10 per cent. solution of potassium iodate in 1 : 2 nitric acid. The precipitate is allowed to settle and the clear liquor decanted through a No. 42 Whatman filter-paper; the precipitate is then rinsed on to the paper with a washing solution made by dissolving 8 g. of potassium iodate in 1 litre of water containing 50 ml. of nitric acid, washed once, rinsed back into the beaker, and churned up with the same solution; it is again returned to the filter, allowed to drain completely, returned to the beaker with hot water, and dissolved by adding concentrated nitric acid while boiling. The solution is treated with 0·25 g. of potassium bromate, and, after cooling, the ceria is reprecipitated by addition of the same amount of iodate-nitric acid solution as that used in the first precipitation. Filtration and washing are carried out as before, except that three washings are given instead of one after the precipitate has been returned to the filter. Paper and precipitate are then transferred to the beaker, 50 ml. of hot water is added, and the mixture is well beaten up and boiled with 7 to 8 g. of oxalic acid until iodine is no longer evolved. After keeping overnight in a cool place the liquid is filtered, and the precipitated cerous oxalate and filter-pulp are thoroughly washed with cold water and ignited to $CeO_2$, which is weighed. The rare earths in the combined filtrates are recovered by boiling with an excess of sodium hydroxide, and the resulting hydroxides are converted into sulphamates or chlorides for the separation of the lanthana from the yttria groups.

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[1] J. Kleinberg, W. A. Taebel, and L. F. Audrieth, *Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 368.

[2] P. H. M. P. Brinton and C. James, *J. Amer. Chem. Soc.*, 1919, **41**, 1080.

($\beta$) *Bromate method.*[1] The neutral nitrate solution of the rare earths is diluted to 200 ml. and boiled with 5 g. of sodium bromate; as soon as bromine vapours begin to appear several small pieces (pea size) of clean marble are dropped in and boiling is continued for several hours, the loss by evaporation being made good by occasional addition of hot water. When a few drops of the filtered solution show no reaction for cerium in the hydrogen peroxide test (see § VI) the marble is removed and the precipitate collected, washed with 2 per cent. sodium nitrate solution, and dissolved in nitric acid with the addition of a few drops of hydrogen peroxide; this solution is evaporated to dryness and the precipitation repeated. The combined filtrates are boiled with more bromate and marble and, if any further precipitate is formed, it is purified by retreatment as before.

(3) *Separation of europium*[2] *(ytterbium) from the other rare earths.* When europium (or ytterbium) chloride is reduced with amalgamated zinc, or electrolytically at a mercury cathode, the bivalent chloride is produced, and this yields a precipitate of the corresponding sulphate on addition of a soluble sulphate. Several repetitions of the process afford an almost complete separation of europium from the terbium group metals or of ytterbium from the most soluble and least basic yttrium group metals. When only small quantities of europium or ytterbium are present, as is usually the case in mineral analysis, the earth mixture must be concentrated by the double sulphate method and then subjected to fractional crystallization. Another method of concentration consists in adding a strontium salt to the chloride solution before reduction; when the sulphate precipitant is added to the reduced solution the strontium sulphate carries down the europous or ytterbous sulphate.

(4) *Approximate separation of praseodymium and neodymium from lanthanum.* The nitrate solution of the cerium-group earths, from which the cerium has been removed by the iodate or bromate method, is evaporated to dryness in a porcelain basin, and the whole is then heated at 450° C. until

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[1] C. James and L. A. Pratt, *J. Amer. Chem. Soc.*, 1911, **33**, 1326.

[2] A. Brukl, *Angew. Chem.*, 1936, **49**, 159; 1937, **50**, 15.

brown fumes cease to be evolved. After cooling, the residue is boiled with water, and the insoluble basic " didymium " nitrate collected and washed with hot water. The filtrate is evaporated and the process repeated; after 2 to 3 repetitions a colourless solution of lanthanum nitrate is obtained, from which the oxide is recovered by precipitation with oxalic acid followed by ignition. The basic " didymium " nitrate on ignition affords a mixture of $Pr_4O_{11}$ and $Nd_2O_3$, which must be ignited and cooled in hydrogen to obtain the sesquioxides for weighing.

According to G. Beck,[1] an approximate separation of praseodymium from neodymium can be obtained by dissolving the oxides in ten times their weight of fused sodium hydroxide in a nickel dish and electrolysing the melt with the dish as anode and a platinum wire as cathode. $PrO_2$ is deposited on the dish, while a little metallic neodymium is formed at the cathode. The clear melt is carefully decanted off, and the residue in the dish extracted with hot water to remove the alkali, and then with 5 per cent. acetic acid to remove neodymium hydroxide. Several repetitions of the process on the insoluble black $PrO_2$ deposit yield a product containing about 90 per cent. $PrO_2$.

Terbia concentrates containing about 50 per cent. $TbO_2$ can be similarly obtained from the terbia group earths; in this case potassium chlorate may be used for the oxidation instead of electrolysis.

The methods described in (3) and (4) are not strictly analytical, but when sufficient material is available they provide approximate means of ascertaining the composition of the mixture.

§ **IV. Gravimetric Determination.**—The rare earths are always weighed as oxides, derived from the oxalates by ignition. Cerous oxalate affords the dioxide $CeO_2$, while the oxalates of the other earths yield the sesquioxide contaminated, if praseodymia or terbia is present, with a certain amount of the corresponding dioxide. Hence the mixed oxides derived from a mineral analysis must be corrected for oxygen in excess of sesquioxide; this may be done by ignition in hydrogen if ceria is absent, or by dissolution in hydrochloric acid and potassium iodide followed by titration of the liberated iodine with thiosulphate if ceria is present. It is better, however, to separate the ceria for accurate work, and use the hydrogen reduction method on the other oxides.

Precipitation of the rare-earth oxalates is best effected in nitric acid solution (5 ml. of concentrated acid per 100 ml. of solution) by the addition of half its volume of a cold saturated solution of oxalic acid; after an hour the solution is stirred vigorously while being heated to boiling, set aside overnight to cool, and filtered. The precipitated oxalates are washed with 2 per cent. oxalic acid solution, transferred to a weighed crucible, and ignited gently at first, and then with the full heat of a good burner. The crucible is covered while cooling, and should be weighed quickly without removing the cover, since all the oxides except ceria absorb moisture and carbon dioxide from the air.

§ **V. Volumetric Determination.**—Volumetric methods have so far been worked out only for cerium and europium; it is possible that ytterbium also can be determined volumetrically by a method similar to that described *below* for europium, since both these metals can be reduced to a bivalent form.

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[1] *Angew. Chem.*, 1939, **52**, 536.

(*a*) *Volumetric Determination of Cerium.*—All the methods proposed depend on the oxidation of cerous to ceric sulphate, followed by reduction of the latter and titration of the excess of reductant. Numerous oxidizing agents have been proposed, but only two have come into general use—ammonium persulphate and sodium bismuthate.

(1) *Persulphate method.*[1] The weighed oxide mixture is transferred to a 100-ml. conical flask, covered with 10 ml. of sulphuric acid and 5 g. of ammonium sulphate, and heated with constant rotation over a free flame so that the acid boils vigorously; the acid first becomes bright orange, due to formation of ceric sulphate, and then colourless or pink with the separation of needle-shaped crystals of double sulphates. At this stage all the oxides should have dissolved; the mixture is allowed to cool, 200 ml. of cold water is added (when a clear solution should be obtained—any residue must be filtered off and retreated), followed by 5 ml. of a 0·25 per cent. solution of silver nitrate and 5 g. of solid ammonium persulphate; the solution is boiled gently for 10 to 15 minutes, by which time the excess of persulphate should be decomposed. The solution is cooled under the tap and treated with a standard solution of ferrous ammonium sulphate until the yellow colour of the ceric sulphate is discharged; the excess of ferrous salt is then titrated with 0·05N. permanganate solution which has been standardized against sodium oxalate in the usual way.

(2) *Bismuthate method.*[2] The oxides are dissolved as described *above*, but more sulphuric acid (10 ml.) is added after cooling, and only 80 ml. of cold water is used to dissolve the sulphates. Oxidation is effected by adding 1 g. of sodium bismuthate and heating the solution to boiling while shaking gently. The hot solution is diluted with 50 ml. of 2 per cent. sulphuric acid, and filtered through an asbestos pad with gentle suction to remove the excess of bismuthate; the pad is washed with about 100 ml. of the dilute acid, and the ceric sulphate in the filtrate is determined with ferrous ammonium sulphate and permanganate as described *above*.

Since the reduction of ceric to cerous sulphate involves a reduction of valency from 4 to 3, 1 ml. of 0·05N-$KMnO_4 \equiv$ 0·008606 g. $CeO_2$.

(*b*) *Volumetric Determination of Europium.*[3]—This process depends on the fact that europium trichloride is reduced to the dichloride by amalgamated zinc, and that the dichloride can be reoxidized to the trichloride by iodine.

The chloride solution, which must be free from oxidizing acids, sulphates and phosphates, is diluted so that the free acidity corresponds to 0·1 to 0·2N. acid, and passed slowly through a Jones reductor containing 20- to 30-mesh amalgamated zinc, the reduced solution being caught in 0·04N. iodine solution; the reductor is washed with 0·1N. hydrochloric acid, and must not be allowed to drain until the zinc is thoroughly washed, since the reduced solution is rapidly oxidized by the air. The excess of iodine is then titrated against 0·04N. thiosulphate solution. 1 ml. of 0·04N. iodine $\equiv$ 0·00704 g. $Eu_2O_3$.

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[1] After von Knorre, *Zeitsch. angew. Chem.*, 1897, **10**, 685, 717; *Ber.*, 1900, **33**, 1924.

[2] F. J. Metzger, *J. Amer. Chem. Soc.*, 1909, **31**, 523.

[3] H. N. McCoy, *ibid.*, 1935, **57**, 1756; 1936, **58**, 1577, 2279.

§ **VI. Detection in Minerals.**[1]—The finely powdered mineral is decomposed by heating with concentrated sulphuric acid or by fusion with potassium bisulphate according to its nature. If decomposition by acid is complete, the cold mass is dissolved in cold water, the solution treated with hydrogen sulphide to remove heavy metals, and filtered; addition to the filtrate of an equal volume of a cold saturated solution of oxalic acid yields a flocculent pale pink to colourless precipitate, which slowly crystallizes, if the mineral contains rare earths, scandia, or thoria. If bisulphate fusion is used to decompose the minerals, the cold melt is boiled with 5 per cent. sulphuric acid until completely disintegrated, and the resulting suspension is poured into an excess of hot 10 per cent. sodium hydroxide solution, which converts all the rare earths, if present, into hydroxides. The washed precipitate is dissolved in hydrochloric acid, any insoluble material filtered off, and the solution treated with oxalic acid as described *above*.

The oxalate precipitate is rinsed into a conical flask and heated with concentrated sulphuric acid until the oxalic acid is completely decomposed; the acid is cooled and diluted, and the earths are precipitated as hydroxides by pouring the solution into 10 per cent. sodium hydroxide. The washed precipitate is dissolved in the minimum of dilute hydrochloric acid with a few drops of hydrogen peroxide, and the solution boiled to destroy the excess of peroxide. Sodium carbonate solution is then cautiously added until a faint permanent precipitate is formed, after which 5 g. of sodium thiosulphate is added, and the solution boiled to precipitate thorium and scandium. The filtrate is once again treated with sodium hydroxide, and the washed precipitate redissolved in hydrochloric acid; this solution is evaporated to dryness on the water-bath, the residue is taken up with a few ml. of water, and 100 ml. of saturated potassium sulphate solution and 5 g. of the solid salt are added. A white to pink precipitate shows the presence of cerium-group metals; addition of oxalic acid to the filtrate produces a white crystalline precipitate if yttria earths are present.

To test for ceria, the double-sulphate precipitate is boiled with sodium hydroxide and the washed precipitate dried in a steam-oven; the colour changes to a dirty violet, and finally a yellow colour develops due to oxidation of cerous to ceric hydroxide. Addition of hydrogen peroxide to the moist hydroxides turns them a deep orange colour if cerium is present.

Other tests for cerium are:

(1) The neutral solution is poured into a large excess of saturated potassium carbonate solution and hydrogen peroxide is added; a yellow to orange colour is produced if cerium is present.

(2) The neutral solution is poured into ammoniacal silver nitrate solution; a brown to black precipitate is produced by cerous salts, since they reduce silver oxide to metallic silver.

(3) The neutral solution is treated with ammonium acetate and hydrogen peroxide; a yellow colour or precipitate of basic perceric acetate is produced; sensitivity: 1 part of ceria in 10,000 parts of solution.

§ **VII. Determination in Ores.**—(*a*) *Decomposition of the Ore.*—(1) *Monazite sand.* The uncrushed sand (10 g.) is heated with 25 ml. of concentrated sulphuric acid at 200° to 250° C. until a thick pasty mass is obtained and no yellow grains can be observed when a small quantity of the paste is stirred into cold water. Decomposition is usually complete in 2 to 3 hours. After cooling, the mass is stirred into 400 ml. of cold water, when everything should dissolve except white grains of zircon or quartz and black grains of rutile. The solution is decanted from the sandy residue into a 500-ml. graduated flask, the residue is washed with cold 5 per cent. sulphuric acid by decantation, the wash liquors are added to the solution in the flask, and the whole is diluted to 500 ml.; the solution is filtered through a dry filter, and 50 ml. ( = 1 g.) of the filtrate are pipetted off for the analysis.

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[1] See also **III**, Table VI, p. 17.

(2) *Silicates.* The very finely ground mineral (2·5 g.) is heated with 10 to 12 ml. of concentrated sulphuric acid as described under (1). The reaction product is dissolved in cold water, the solution is made up to 250 ml. in a graduated flask, and 100 ml. ( = 1 g.) is pipetted off.

(3) *Niobates and titanoniobates.* These minerals are best decomposed by hydrofluoric acid (*f*, *below*).

(*b*) *Separation of the Total Rare Earths.*—The solution obtained under (*a*) is treated cold with an equal volume of a cold saturated solution of oxalic acid. The mixture is set aside for an hour, then stirred vigorously, and left overnight. The oxalate precipitate is collected, washed with cold 2 per cent. oxalic acid solution, and ignited. The resulting oxides are dissolved in hydrochloric acid with the aid of a little hydrogen peroxide; if the mineral contains phosphates a second precipitation with oxalic acid is necessary to complete the removal of the phosphoric acid, and if the mineral contains lime a precipitation with ammonia is necessary to eliminate that carried down by the oxalate precipitate. In the latter case the chloride solution is boiled with 5 g. of ammonium nitrate and just sufficient ammonia to make the solution ammoniacal, cooled completely, treated with a further 10 ml. of ammonia, and filtered cold on a No. 41 Whatman paper; the precipitate is washed with ammoniacal 2 per cent. ammonium nitrate solution and dissolved in the minimum amount of nitric acid. The second oxalate precipitate obtained in the analysis of phosphate minerals is ignited, and the oxides are dissolved by heating on the water-bath with concentrated nitric acid, with the occasional addition of a few drops of 6 per cent. hydrogen peroxide until a clear pink solution is obtained.

(*c*) *Removal of Thorium.*—The nitrate solution is evaporated to dryness on the water-bath, the residue well stirred until it ceases to smell of acid, moistened with water and again dried, and finally dissolved in 100 ml. of warm 10 per cent. ammonium nitrate solution; the thoria is then precipitated by addition of hydrogen peroxide (**XV**, § III, *a*). The precipitate is dissolved in nitric acid, and reprecipitated.

(*d*) *Separation and Determination of the Cerium.*—The combined filtrates from the thoria are boiled to decompose excess of hydrogen peroxide, evaporated to 200 ml., and treated with oxalic acid. The oxalate precipitate is washed and ignited to obtain the oxides which are dissolved in nitric acid and hydrogen peroxide; the ceria is then separated by the iodate method (§ III, *d*, 2, *a*).

(*e*) *Separation and Determination of the Other Rare Earths.*—The combined filtrates from the iodate precipitates are boiled with an excess of sodium hydroxide, and the resulting hydroxides are collected, washed with hot water, and dissolved in hydrochloric acid. The chloride solution is evaporated to dryness, the residue dissolved in a few ml. of water, and the lanthanum group precipitated by addition of saturated potassium sulphate solution and a few grams of the solid salt (§ III, *d*, 1, *a*). The precipitate is converted into hydroxides by digestion with sodium hydroxide, the hydroxides are dissolved in hydrochloric acid, and the potassium sulphate precipitation is repeated. The lanthana earths in the precipitate and the yttria earths in the filtrate are then separately converted into oxides by way of the hydroxides, chlorides, and oxalates; the oxides are ignited and cooled in hydrogen, and the residual sesquioxides weighed. Further separations can be made only if several grams of oxide mixture are available (see § III, *d*, 3 and 4).

(*f*) *Determination of Rare Earths in Titanoniobates.*[1]—The finely ground mineral is dissolved in cold hydrofluoric acid, which is evaporated on a water-bath; the moist residue is taken up in 100 ml. of water, and the insoluble rare-earth fluorides are collected in a rubber funnel, washed with cold water, rinsed back into the platinum dish, and converted into sulphates by evaporation with sulphuric acid. The residue is heated at 450° C. until fumes of acid cease to be evolved, and dissolved in cold water; the earths are separated into groups by addition of potassium sulphate, and the ceria is then determined in the precipitate by the method given *above*.

§ **VIII. Complete Analysis of Monazite.**—10 g. of the uncrushed sand is heated with 20 ml. of concentrated sulphuric acid, and the product is dissolved in 300 ml. of cold water. The solution is saturated with hydrogen sulphide and filtered into a 500-ml. graduated flask, the insoluble material washed with cold 5 per cent. sulphuric acid saturated with hydrogen sulphide, and the filtrate diluted to the mark. Aliquot parts of this solution are taken for the determination of the soluble constituents, while the insoluble material is analysed for lead, silica, and "sand" (zircon, rutile, garnet, etc.) as described under (*b*), *below*.

(*a*) *Solution.*—(1) *Determination of the rare earths.* 50 ml. of the solution is precipitated with oxalic acid, the oxalates are converted to oxides, the oxides dissolved in hydrochloric acid, and the oxalates again precipitated. This second precipitate is used for the determination of thoria, ceria, and rare earths as described in § VII.

(2) *Determination of the other soluble bases.* The oxalate filtrates from (1) are made just ammoniacal with ammonia and treated with 1 g. of tannin dissolved in a little water, which precipitates as oxalates, phosphates or tannin complexes all the bases likely to be present. The precipitate is mixed with a little filter-pulp, filtered under gentle suction, washed with hot 2 per cent. ammonium nitrate, and ignited in a platinum crucible. The residue is fused with 2 to 3 g. of sodium carbonate, the melt leached with hot water, and the insoluble material filtered off, washed with 2 per cent. sodium carbonate solution until free from phosphate, rinsed back into the

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[1] J. L. Smith, *Amer. Chem. J.*, 1883, **5**, 73.

beaker, and digested with concentrated hydrochloric acid. After dilution and addition of filter-pulp and ammonium chloride, the iron and titania are precipitated with ammonia, and the filtrate is used for the determination of lime. The hydroxide precipitate should be ignited and again fused with sodium carbonate to remove the last traces of phosphoric acid; the residue from this process is used for the determination of iron oxide, and titania if present, by the usual methods. The two sodium carbonate filtrates contain the alumina, which is recovered and weighed as $AlPO_4$.

(3) *Determination of magnesia.* 100 ml. ( = 2 g.) of the original solution is saturated with potassium sulphate by stirring in the powdered salt, and the precipitate collected, washed with saturated potassium sulphate solution, and rejected. The filtrate is boiled with an excess of sodium hydroxide solution, and the precipitate collected, washed with 1 per cent. sodium hydroxide, and dissolved in dilute hydrochloric acid. About 0·5 g. of ferric alum is added to the solution, which is then boiled with ammonium chloride and a large excess of ammonia; repetition of the precipitation affords a combined filtrate containing all the magnesia and most of the lime. The determination is finished in the usual way.

(4) *Determination of phosphoric acid.* 100 ml. of the solution is transferred to a 200-ml. graduated flask and saturated with potassium sulphate, the flask is filled to the mark with a saturated solution of the same salt and, after well mixing the solution, it is set aside overnight, then filtered through a dry paper. 50 ml. of the filtrate is pipetted into a beaker and treated with a saturated solution of 5 g. of citric acid and sufficient strong ammonia to neutralize the solution and provide an excess equal to one-fifth of the total volume of solution. The phosphoric acid is then precipitated with magnesia mixture; the washed precipitate is dissolved and reprecipitated before being ignited to pyrophosphate for weighing.

(*b*) *Analysis of the Insoluble Material.*—The lead sulphide is removed by digestion with dilute nitric acid, and the lead determined as sulphate or molybdate. . The residue from the lead extraction is rinsed back into a platinum dish and the free silica (*i.e.* that present in the monazite) removed by digestion with 5 per cent. sodium hydroxide; the silica is recovered by evaporation with hydrochloric acid, etc. The insoluble sand is washed with hot water, ignited, weighed, and analysed by the methods described for zircon sand (**XIV**, § VII, *b*).

## XIII.—TITANIUM.

§ **I. Minerals.**—(*a*) *Oxides.*—Titanium dioxide, $TiO_2$, the only naturally occurring oxide, is found in three distinct crystalline modifications:

(1) *Rutile* crystallizes in the tetragonal system, and is isomorphous with tinstone, thorite, and zircon. It occurs as reddish-brown to black prisms, terminated by pyramids, the sides of the prisms being vertically striated. Twins are common. Brittle, fracture sub-conchoidal; sub-metallic to adamantine lustre. Streak pale brown. H. 6·5; sp. gr. 4·2.

(2) *Anatase* or *octahedrite* is a distinct tetragonal form crystallizing in pyramids or tables. H. 5·5; sp. gr. 3·8 to 4·0.

(3) *Brookite*, the orthorhombic variety of the dioxide, crystallizes in short tabular prisms. H. 6; sp. gr. 3·9 to 4·2.

(*b*) *Titanates.*—(1) *Ilmenite* is an iron-black mineral with sub-metallic lustre, essentially a ferrous titanate, but of very variable composition, ferric oxide often partly replacing the titanium dioxide. Rhombohedral tables; conchoidal fracture; brownish-black streak; magnetic to weak electromagnet. H. 5·5; sp. gr. 4·5 to 5·0.

*Iserine* and *menaccanite* are varieties of ilmenite occurring in alluvials.

(2) *Pseudobrookite*, ferric titanate, $2Fe_2O_3.3TiO_2$, occurs as dark brown to black, sub-translucent, horizontally striated tables belonging to the orthorhombic system. Streak yellow to brown. H. 6; sp. gr. 4·4.

(3) *Pyrophanite*, manganese titanate, $MnTiO_3$, crystallizes in the rhombohedral system as deep blood-red, transparent tables, giving an ochre-yellow streak with a tinge of green. H. 5; sp. gr. 4·5.

(4) *Perovskite*, calcium titanate, $CaTiO_3$, occurs in pale yellow to red-brown cubes with an adamantine lustre; transparent to opaque, brittle. H. 5·5; sp. gr. 4.

(*c*) *Titanosilicates.*—(1) *Sphene* or *titanite*, calcium titanosilicate, $CaSiTiO_5$, occurs variously coloured: yellow, brown, green, red, or black. Transparent to opaque mineral crystallizing in the monoclinic system. Lustre resinous to adamantine. Twins common. Also found massive. H. 5·5; sp. gr. 3·5.

(2) *Guarinite* is a yellow translucent orthorhombic variety of calcium titanosilicate crystallizing in thin tables with an adamantine lustre. H. 6; sp. gr. 3·5.

(*d*) In addition to the above, titanium occurs in many rare and unimportant silicates of very complex composition, which usually contain the rare earths, thorium, or zirconium. It is also an essential constituent of various titanoniobates, such as the *euxenite-polycrase* series (see **XVIII,** § I, *b*). As a subordinate constituent it is present in most rocks, especially the more basic ones, and in clays, as well as in bauxite.

§ **II. Properties and Compounds.**—(*a*) The *metal* has a brilliant white colour, and is very brittle and hard. It has a powerful affinity for carbon, oxygen, and nitrogen, and therefore is very difficult to prepare pure, although it can be made by reducing the dioxide with carbon in the electric furnace in the absence of air. Workable titanium has been prepared by thermal dissociation of the tetriodide. It is soluble in acids, and decomposes steam at a red heat. Sp. gr. 4·87; melting-point 1800° C.

(*b*) The *dioxide* is trimorphous (see § I, *a*). As usually obtained artificially, it is a white amorphous powder, insoluble in water, hydrochloric or nitric acid, and only with difficulty soluble in concentrated sulphuric acid. Rendered soluble by fusion with bisulphate. Readily obtained by igniting the precipitate produced by ammonia in a solution of a titanium salt. Turns a vivid yellow when heated.

(*c*) *Orthotitanic acid*, $H_4TiO_4$,[1] is precipitated from a *cold* hydrochloric-acid solution of a titanium salt on the addition of alkalis as a voluminous white precipitate readily soluble in dilute acids. On long standing under water it gradually changes to metatitanic acid, and, on ignition, yields the dioxide with the evolution of light.

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[1] In accordance with the view still generally held, we have maintained the distinction between ortho- and metatitanic acid, although it is no doubt more correct to regard titanic acid as a hydrated oxide, $TiO_2.xH_2O$, containing an indefinite amount of water which varies with the conditions under which the precipitate is formed, and determines its solubility in acids. (*Cf.* R. J. Meyer and O. Hauser, *Die Analyse der seltenen Erden und der Erdsäuren*, Stuttgart, 1912, p. 125.)

(*d*) *Metatitanic acid*, $H_2TiO_3$,[1] is produced by boiling a nearly neutral hydrochloric-acid solution of the ortho-acid as a white voluminous precipitate. On ignition it is converted into the anhydride without evolution of light. It is insoluble in acids, with the exception of hot strong sulphuric or hydrofluoric acid.

(*e*) *Sodium Titanates.*—Three compounds, *viz.* $Na_2Ti_2O_5$, $Na_2Ti_3O_7$, and $Na_4Ti_3O_8$, are produced by fusion of the dioxide with sodium carbonate. They are insoluble in water.

(*f*) *Titanium peroxide*, $TiO_3$, is produced when hydrogen peroxide acts on a sulphuric-acid solution of the dioxide. It gives an intense orange-brown solution in acids, which decomposes on boiling.

(*g*) *Titanium Sesquioxide*, $Ti_2O_3$.—Salts of this oxide (*e.g.* titanous chloride, $TiCl_3$) are produced by the reduction of quadrivalent titanium in acid solution with zinc. Their solutions are of a deep violet colour, and, being readily oxidized, are powerful reducing agents.

(*h*) *Titanium Tetrafluoride*, $TiF_4$.—When titanic acid is dissolved in hydrofluoric acid, hydrogen fluorotitanate, $H_2TiF_6$, is believed to be formed. Unlike silicon, titanium is not volatilized by evaporation of hydrofluoric-acid solutions in the presence of sulphuric acid, but if the latter is omitted a considerable proportion of the titanium is volatilized.

(*i*) *Potassium fluorotitanate*, $K_2TiF_6.H_2O$, is produced by the addition of potassium fluoride to a solution of the preceding compound. Ninety-six parts of water dissolve 1 part of the anhydrous salt at ordinary temperature.

(*j*) *Titanic Sulphates.*—The normal salt, $Ti(SO_4)_2$, has not been isolated, but several titanyl sulphates are known. Titanic acid is soluble in sulphuric acid, while the oxide dissolves in fused bisulphate. The neutralized solution is gradually and completely hydrolysed when boiled, metatitanic acid being precipitated.

§ **III. Quantitative Separation.**—Important developments in the analytical chemistry of titanium have taken place during the past few years as the result of our discovery of the precipitability of the earths by tannin from tartrate solution,[2] and of a serial order of tannin precipitation from oxalate solution.[3]

We proved that tannin acts as a general group reagent for all the earths by precipitating them from neutralized tartrate solution; in the case of some elements (*e.g.* beryllium, manganese, rare earths, etc.) precipitation takes place only in ammoniacal tartrate solution.

In oxalate solution, a more pronounced differentiation in chemical behaviour between certain groups of elements becomes evident. We have shown that tantalum, titanium, and niobium (in the order named) are more readily precipitated by tannin (that is, at a higher acid concentration) than are vanadium, ferric iron, zirconium, thorium, uranium, aluminium, etc. The rare earths, the oxalates of which are insoluble in ammonium oxalate solution, are not included in the series. We distinguish between the *acid tannin group*, or *Group A*, comprising the earth acids and titania, and the *basic tannin group*, or *Group B*, containing the rest of the above-named elements. A number of accurate quantitative separation processes have been worked out on the basis of the reactions here discussed.

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[1] See footnote on p. 87.

[2] W. R. Schoeller and A. R. Powell, *Analyst*, 1928, **53**, 264; W. R. Schoeller and H. W. Webb, *ibid.*, 1929, **54**, 709; 1933, **58**, 143.

[3] W. R. Schoeller and A. R. Powell, *ibid.*, 1932, **57**, 550; W. R. Schoeller and H. W. Webb, *ibid.*, 1936, **61**, 585; Schoeller, *op. cit.*, p. 148.

For example, the separation of titanium from zirconium, thorium, and aluminium, for which three distinct processes were required, can now be accomplished in one operation. Although tannin does not separate titania from the earth acids in oxalate solution, a separation can be effected in a medium containing free sulphuric acid[1]; hence tannin can be employed as a specific reagent for titania as well as for the earth acids. In this respect it is greatly superior to cupferron, which precipitates all the above earths, leaving only aluminium and uranium in solution.

(*a*) *From Metals of the Hydrogen-sulphide Group.*—Whilst titanium is not precipitated as sulphide, it should be borne in mind that hydrogen sulphide in hot, rather feebly acid solution acts as a flocculating agent in promoting hydrolysis of titanic salts, with precipitation of titanic acid. The sulphate solution should, therefore, be rather strongly acid (at least 0·3N.) or, preferably, contain tartaric acid to prevent contamination of the sulphide precipitate with titanic acid.

(*b*) *From Tin.*—(1) *Titania preponderates.* When the mixed oxides are fused with potassium bisulphate and the melt is digested with tartaric acid solution, the titania dissolves completely whilst stannic oxide remains largely unaffected. The few mg. of tin that may be rendered soluble in the fusion are precipitated from the unfiltered tartrate solution by means of hydrogen sulphide. The mixed precipitate of stannic oxide and sulphide is collected, washed with hydrogen-sulphide water containing a little sulphuric acid, and ignited to $SnO_2$. The titania in the filtrate is recovered by precipitation with tannin or cupferron.

(2) *Tin oxide preponderates.* The mixed oxides are heated to low redness in a current of hydrogen (Rose crucible or porcelain boat), and the reduced tin is dissolved in 20 per cent. hydrochloric acid.[2] The residue is collected, washed with dilute hydrochloric acid followed by water, ignited, and treated as indicated under (1), *above*. We think it advisable to test the tin solution for traces of dissolved titania by eliminating the tin as sulphide and precipitating the filtrate with tannin.

(*c*) *From Iron, Zinc, Nickel, Cobalt, and Manganese.*—(1) *Ammonium sulphide method.* The acid chloride or sulphate solution of the metals is treated with hydrogen sulphide to reduce ferric iron. Tartaric acid (four times the weight of the metallic oxides present) is added, and the solution is rendered ammoniacal. Hydrogen sulphide is again passed through the solution to precipitate the metallic sulphides; the solution is warmed to promote flocculation, and set aside overnight. The precipitate is collected and washed with dilute ammonium sulphide solution containing ammonium nitrate.

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[1] W. R. Schoeller, *Analyst*, 1929, **54**, 453.

[2] A. Hilger and H. Haas, *Ber.*, 1890, **23**, 458.

The filtrate is boiled with excess of dilute sulphuric acid until hydrogen sulphide is expelled. If the quantity of titania present is moderate to small (*e.g.* 0·1 g.), it is recovered by precipitation with cupferron or tannin; if large, the tartaric acid is destroyed by evaporation with nitric and sulphuric acids,[1] and the titania is determined in the diluted and filtered solution by precipitation with ammonia (§ IV, *a*).

For the quantitative recovery of manganese by this procedure, the tartrate solution should have been concentrated to about 25 ml. prior to precipitation of the sulphides.[2]

Manganese can also be separated from titanium by double precipitation of the latter with ammonia and ammonium chloride.[3]

If the above procedure is applied to substantial quantities of iron and titanium, we advise retreating the ferrous sulphide precipitate. Filter and precipitate are heated in a silica crucible on an asbestos mat until the paper is charred, and the residue is ignited to ferric oxide, which is fused with bisulphate; the melt is dissolved in tartaric acid solution, and precipitation of the ferrous sulphide repeated.

In this process, citric acid may be substituted for tartaric acid. The citric-acid complexes of the earths are held [4] (perhaps on the strength of insufficient experimental evidence) to be more stable than the corresponding tartaric-acid compounds. Tannin and cupferron precipitations proceed equally well in citrate and in tartrate solutions.

(2) *Thiosulphate method.*[5] The acid sulphate solution is treated with hydrogen sulphide to reduce ferric iron, and the cold solution is treated with sodium carbonate solution until the precipitate thus formed begins to redissolve slowly. A permanent precipitate must be avoided. A solution of 10 g. of sodium thiosulphate in cold water is then added, and the liquid gently boiled for half an hour, the water lost by evaporation being replaced. The precipitate is collected, washed with hot water, and ignited to $TiO_2$, which should be leached with acidulated water to remove alkali. It is advisable to fuse the oxide with bisulphate and to repeat the precipitation.

(3) If considerable iron has to be removed, it may be extracted with ether, as in steel analysis.

(*d*) *From the Earths of Group B* (*Alumina*, *Zirconia*, *Hafnia*, *Thoria*) *and Chromium*, *Iron*, *Uranium*, *Vanadium*, *Manganese*, *Beryllium: Authors' Tannin Method.*—(*Note.*—If more than 0·05 g. of iron is present, the dark colour of the iron-tannin complex renders the observation of the colour changes rather difficult; hence it is advisable to remove the iron as ferrous sulphide in tartrate solution (*c*, 1, *above*) before applying the tannin method.)

Minerals or mixed oxides are fused with potassium bisulphate; the quantity taken is adjusted to a maximum of 0·2 to 0·25 g. $TiO_2$. The cold melt is dissolved in hot ammonium oxalate solution (60 to 100 ml.), and any insoluble matter (silica) is filtered off. If the substance is in mineral or tartaric acid solution, 3 to 5 g. of ammonium oxalate is added to the hot solution and dissolved by heating.

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[1] W. M. Thornton, Jr., *Titanium*, New York, 1927, p. 98.

[2] W. R. Schoeller and H. W. Webb, *Analyst*, 1934, **59**, 667.

[3] G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1923, **45**, 676.

[4] L. J. Curtman and H. Dubin, *ibid.*, 1912, **34**, 1485; W. M. Thornton, Jr., *op. cit.*, pp. 95, 162.

[5] M. Dittrich and S. Freund, *Zeitsch. anorg. Chem.*, 1907, **56**, 337.

The boiling solution (150 to 200 ml.) is well stirred and cautiously treated with ammonia to the appearance of a faint cloudiness, which is immediately removed with a minimum of dilute hydrochloric acid. In the case of tartrate solutions, a strip of litmus-paper dropped into the liquid serves as indicator. The solution, which should be slightly acid to litmus, is now treated with 5 drops of strong hydrochloric acid, after which the solution is diluted with an equal volume of saturated ammonium chloride solution.

The liquid is boiled, stirred, and precipitated drop by drop with freshly made 5 per cent. tannin solution. The amount of tannin should be about 15 times that of the titania. The solution is boiled for a minute or two after addition of the reagent, and the beaker is transferred to a hot-plate, when the flocculent, orange-red titanium-tannin precipitate will gather into clouds, leaving part of the liquid clear. If this shows an orange tint, the precipitation of the tannin complex is probably incomplete; further cautious addition of tannin reagent with brisk agitation will increase the precipitation, the solution turning straw-yellow.

If, on the other hand, the liquid is pale yellow, or if it is mauve, pale brown, or greyish-blue (due to iron, uranium, or vanadium, respectively), no further addition of tannin is necessary.

After one hour on the hot-plate, the liquid is filtered under slight suction through an 11- or 12·5-cm. No. 40 Whatman filter containing a little filter-pulp. The precipitate is returned to the beaker with 100 ml. of hot wash-liquor (containing 5 per cent. of ammonium chloride and 1 per cent. of oxalate) and well churned up until all the clots are broken up. The suspension is returned to the filter, and the beaker is cleaned with a rubber-tipped glass rod and filter-pulp. When the washing is completed, the precipitate, $P^1$, is compressed by suction and ignited wet in a tared silica crucible.

The filtrate from $P^1$ should always be tested for complete precipitation by evaporation to 300 to 400 ml., addition of another 0·5 g. of tannin, followed by N. ammonia added drop by drop to the boiling solution until a slight precipitate is produced. If this is dirty grey (Zr, Th, Al, Be), mauve (Fe), brown (U), or bluish-black (V), and readily soluble upon re-acidification with N. hydrochloric acid, the titanium precipitation is complete. If, however, the precipitate still shows an orange tint, more N. ammonia is added to complete the precipitation of titanium. In this case, the second precipitate, $P^{1a}$, is collected and added to $P^1$, while the filtrate is again tested as before.

A more certain test for complete precipitation consists in collecting, washing, and igniting the discoloured small precipitate produced as explained *above* and containing the balance of the titania, if any. The discoloured residue so obtained is fused with bisulphate, and the whole process repeated: the orange-red colour of the small tannin precipitate thus obtained is a very delicate test for titanium.

The tannin precipitate or combined precipitate, after strong ignition, is digested on a hot-plate with hydrochloric acid (1 : 2 water) for half an hour.

It is then transferred to a small beaker, and the solution made ammoniacal. The precipitate is collected on an ashless filter, washed with ammonium chloride solution, ignited wet, and weighed as $TiO_2$.

The purity of the weighed precipitate may be ascertained by fusion with bisulphate, solution of the melt in ammonium oxalate solution, neutralization, and reprecipitation with an amount of tannin equal to 15 times that of the weighed titania. The filtrate from the tannin precipitate should, of course, be tested for complete precipitation of the titania as described *above*. In separations from substantial amounts of Group B elements, the weight of the second titania precipitate may be a few mg. lower than that of the first owing to the removal of the coprecipitated elements.

If the mineral under examination contains niobium and tantalum, these elements are quantitatively precipitated with the titania. For their determination in the weighed mixed oxides, see **XVIII**, § III, *h*.

(*e*) *From Aluminium, Chromium, Uranium, Manganese, Nickel, Cobalt, Zinc, Beryllium, Phosphoric Acid: Cupferron Method.*[1]—The operation is carried out in strongly acid sulphate solution, and the presence of tartaric (citric) acid is immaterial. Hence filtrates from ferrous and other sulphides precipitated in ammoniacal tartrate solution (*c*, 1, *above*) can be treated by this process, after having been acidified, boiled, and cooled. The reagent is a filtered solution of cupferron, usually 6 per cent., freshly prepared with cold water. The titania to be determined should not greatly exceed 0·2 g.

The solution of the metals is diluted to 400 ml., and acidified with 40 ml. of sulphuric acid (1 : 1). It should be cooled to 10° to 15° C. The solution is well stirred and the reagent added drop by drop until the yellow precipitate coagulates, leaving the liquid clear. This is tested for complete precipitation by addition of more reagent: the formation of a transient white precipitate of nitrosophenylhydroxylamine proves that all of the titania has been precipitated. A large excess of reagent is required.

A fairly large proportion of filter-pulp is stirred into the suspension, which is at once filtered with the aid of moderate suction. The beaker is cleaned, and the precipitate well washed with cold N. hydrochloric acid containing a little cupferron. When the washing has been completed, the vacuum is increased with the object of dehydrating the mixed precipitate and pulp as thoroughly as possible. This treatment and the incorporation of filter-pulp with the precipitate facilitate its ignition by preventing liquefaction and effervescence during ignition. Filter and precipitate are transferred to a tared porcelain or silica crucible and heated on an asbestos mat under a hood until organic vapours cease to be evolved. The crucible is then heated more strongly until the carbon is burned away, and finally over a blast-burner. The $TiO_2$ is weighed.

If the ignited precipitate is bulky, it is advisable to digest it with hot dilute hydrochloric acid followed by ammonia in the manner described for tannin precipitates (*d*, *above*), and to ignite and weigh again.

The cupferron method does not provide a separation of titanium from iron, zirconium, vanadium, niobium, or tantalum, which are quantitatively precipitated, while thorium, the rare earths, and tungsten are coprecipitated to a certain extent. The separation of titanium from small quantities of phosphoric acid is satisfactory.

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[1] W. M. Thornton, Jr., *op. cit.*, pp. 90, 107.

If it is intended to determine the metals in the cupferron filtrate, this is evaporated to small bulk with excess of nitric acid; tartaric acid, if present, may be destroyed at the same time by evaporation to fumes of sulphuric acid and cautious addition of strong nitric acid until the black foaming mass has become colourless.

(*f*) *From Chromate, Vanadate, Molybdate, Phosphate: Sodium Carbonate Fusion.*—The ore, or the mixture of oxides, is fused with sodium carbonate (and nitrate if chromium is present), and the melt extracted with boiling water. The insoluble sodium titanate is filtered off, washed with hot water, ignited in the platinum crucible previously used, and again fused with sodium carbonate, etc. The extracts are combined. A third fusion may be necessary; the separation is complete when the alkaline filtrate after neutralization with nitric acid gives no precipitate with mercurous or silver nitrate.

The residue from the last fusion is returned to the beaker together with the filter, the paper is pulped, and the mixture is digested with hot, dilute hydrochloric acid. The liquid is made ammoniacal, and the titania is collected, washed with ammonium chloride solution, and ignited.

(*g*) *From Tungstate.*—When the fusion procedure described under (*f*) *above* is applied to a mixture of titanic and tungstic oxides, the residue from the extraction with water may retain as much as 40 per cent. of the tungsten. We have obtained correct results by the following process [1]:

The mixed oxides are fused with sodium carbonate in a platinum crucible over a blast-burner for 20 minutes, or until a clear melt is obtained. The crucible is transferred to a nickel dish containing a solution of 10 g. of sodium hydroxide in 50 ml. of water, and digested on a steam-bath in the covered dish for 2 to 3 hours, with occasional stirring and addition of water to replace evaporation loss. The crucible is withdrawn, and well cleaned with 50 ml. of water; the liquid is set aside till cold, filtered, and the insoluble residue, $P^1$, washed with half-saturated sodium chloride solution.

The filtrate is heated on a steam-bath after addition of phenolphthalein and sufficient dilute hydrochloric acid to discharge the red colour (bicarbonate stage). The cautious addition of dilute acid is continued from time to time as the colour of the indicator is restored by loss of carbon dioxide. When the small amount of titania present in the filtrate has flocculated ($P^2$), it is collected and washed in the same manner as $P^1$. The filters containing the two precipitates are pulped with dilute hydrochloric acid and heated, the liquid is made ammoniacal, and the titania is collected, washed, and ignited.

The process for the separation of titania from tungstic oxide by fusion with bisulphate and extraction of the melt with water, described in some text-books, has been found by us [1] to be quite unreliable, no precipitate of tungstic acid being obtained with quantities of as much as 0·05 g.

(*h*) *From Silica.*—(1) *Silica preponderates.* The silica is volatilized by evaporation with hydrofluoric acid and more than enough sulphuric acid to combine with the titania. When the silicon fluoride has been volatilized, the residual mass is heated until the free sulphuric acid has been expelled, then over a strong burner to decompose the titanic sulphate, and the residue is weighed as titania. Alternatively, the acid sulphate mass freed from silicon fluoride is fused with bisulphate if it is intended to obtain the titanium in solution.

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[1] A. R. Powell, W. R. Schoeller, and C. Jahn, *Analyst*, 1935, **60**, 506.

(2) *Titania preponderates.* The material is fused with potassium bisulphate, and the cooled melt is dissolved in dilute sulphuric acid, with or without addition of tartaric acid or ammonium oxalate. The extract is filtered, the residue collected, washed with dilute sulphuric acid, ignited in a tared platinum crucible, and weighed. It is then treated with hydrofluoric and sulphuric acids as described under (1) *above.* Any slight residue from this treatment is again fused with bisulphate, and the solution of the melt is added to the main portion.

(*i*) *From Thorium.*—See **XV,** § III.

(*j*) *From Rare Earths.*—See **XII,** § III, *a.*

(*k*) *From Zirconium and Hafnium.*—See **XIV,** § III, *c* and *e.*

(*l*) *From Niobium and Tantalum.*—See **XVIII,** § III, *h.*

§ **IV. Gravimetric Determination.**—Titanium is always weighed as the dioxide, after precipitation by one of the procedures enumerated *below.* If the ignited precipitate is at all bulky, it should be transferred from the crucible (silica, porcelain, or platinum may be used) to a small beaker and digested hot with hydrochloric acid (1 : 2 water) for about half an hour. The liquid is made ammoniacal, and the precipitate is collected, washed, ignited strongly, and weighed.

(*a*) *Ammonia.*—Pure titanium solutions are heated to boiling and treated with a slight excess of ammonia. The colourless flocculent precipitate is mixed with a little filter-pulp, allowed to settle, collected, washed with hot 2 per cent. ammonium chloride or nitrate solution, and ignited wet in a tared crucible.

(*b*) *Tannin in Oxalate Solution.*—The precipitation of the red tannin adsorption complex has been described under § III, *d, above.* Tannin precipitation is very advantageous for micro-work on account of the bulky nature and characteristic colour of the precipitate.

(*c*) *Tannin in Tartrate Solution.*[1]—The tartrate solution containing 30 ml. of hydrochloric acid or its equivalent in ammonium chloride is made slightly ammoniacal to litmus-paper, boiled until the excess of ammonia is expelled, and treated while boiling with a freshly made solution of tannin (20 times the weight of the titania) and 5 g. of ammonium acetate. The precipitate is left to settle on a hot-plate or steam-bath, collected under slight suction, and further treated as described under § III, *d, above.*

(*d*) Titanium is precipitated by *cupferron* (§ III, *e*), the yellow precipitate upon ignition leaving the dioxide.

(*e*) *Thiosulphate Hydrolysis.*—The cold acid solution is nearly neutralized with sodium carbonate, and boiled with 10 g. of sodium thiosulphate for half an hour, the volume of the solution being kept constant. The precipitate, consisting of titanic acid and sulphur, is mixed with filter-pulp, collected, well washed with hot water, and ignited (*cf.* § III, *c*, 2, *above*).

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[1] Schoeller, *op. cit.*, p. 160.

This mode of precipitation has been almost superseded by the preceding, because the precipitate produced by thiosulphate is apt to retain alkali and hence requires careful lixiviation. However, it is useful in certain cases, *e.g.* when large quantities of titania have to be recovered, in which case the tannin and cupferron precipitates would be inconveniently bulky. Thiosulphate hydrolysis also permits of the simultaneous recovery of titania, zirconia, thoria, and alumina (precipitation of alumina is not always quantitative).

(*f*) The time-honoured hydrolysis procedure from feebly acid sulphate solution is now out of date, although still described in some Continental manuals.[1] It consists in boiling the largely diluted solution under reflux for some hours, sulphurous acid being added from time to time. The complete precipitation of the titania is difficult to ascertain, the precipitate is impure, and it filters badly owing to its slimy nature.

§ V. **Volumetric Determination.**—Titanic salts in acid solution are reduced by zinc to the tervalent condition, and an accurate volumetric process based on this reaction has been worked out by G. E. F. Lundell and H. B. Knowles.[2]

(*a*) The titanium sulphate solution, which must be free from other reducible metals (*e.g.* iron, chromium, vanadium, uranium), is diluted to 150 ml., the acidity being adjusted to between 3 and 5 per cent. of sulphuric acid by volume. The cold solution is passed through a Jones reductor of 19 mm. bore containing a 43-cm. column of amalgamated zinc. The reductor is washed immediately before use with dilute sulphuric acid; the receiver is emptied, rinsed, and filled with ferric sulphate solution (from 3 to 5 times in excess of the quantity required for oxidation:

$$Ti_2(SO_4)_3 + Fe_2(SO_4)_3 = 2Ti(SO_4)_2 + 2FeSO_4\ ).$$

For the determination, the following solutions are passed through the reductor: 25 to 50 ml. of dilute sulphuric acid (3 to 5 per cent.), the titanium solution, another 100 ml. of the dilute acid, and 100 ml. of water. The reduction is effected at a speed of 100 ml. per minute. It is unnecessary to expel the air from the solutions or the receiver. When the liquids have been passed through the reductor, the solution of ferrous salt in the receiver is titrated with 0·1N. permanganate solution standardized against sodium oxalate. A blank is run with the quantities of reagents used in the assay. Conversion factors: $Na_2C_2O_4$ to $TiO_2$, 1·1926; $Na_2C_2O_4$ to Ti, 0·7150.

(*b*) *Titration in Presence of Iron.*—If titanium is to be determined in the presence of iron, the above process must be modified by omitting the ferric sulphate solution from the receiver and maintaining an atmosphere of hydrogen or carbon dioxide therein. The reduced solution is titrated with a solution of ferric alum (14 g. per litre) after addition of 5 ml. of saturated ammonium thiocyanate solution. The end-point is indicated by a pale red tinge. The ferric alum solution is standardized against a weighed amount of pure titania, which is fused with bisulphate and dissolved in the same amount of dilute sulphuric acid as the assay.

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[1] E.g. *Ausgew. Methoden*, p. 164.

[2] *J. Amer. Chem. Soc.*, 1923, **45**, 2620.

§ **VI. Colorimetric Determination.**—Titanic sulphate yields intense orange-yellow solutions on the addition of hydrogen peroxide. The reaction has been made the basis of a colorimetric method by E. Weller.[1] The colour is best compared when it is of a deep straw-yellow tint, corresponding to less than 0·0010 g. of titania per 100 ml. of test solution. It is bleached by hydrofluoric acid even in minute quantity, and by large amounts of phosphoric acid and potassium sulphate, but the presence of considerable free sulphuric acid tends to overcome the interference of the latter, which is present from the bisulphate fusion. Uranium, vanadium, molybdenum, and chromates interfere by giving a colour with the peroxide. Iron interferes if present in quantity; the yellow tint is discharged by phosphoric acid, due to the formation of ferric phosphate, but the acid itself has a slight bleaching affect (*above*). Therefore it is best to proceed as follows:

The titanium solution is treated with 5 ml. of phosphoric acid (sp. gr. 1·38), 5 ml. of 6 per cent. hydrogen peroxide, and 9 ml. of strong sulphuric acid, and diluted to 100 ml. in a Nessler tube. A standard tube is prepared with the same quantities of reagents as the assay, including potassium sulphate, and diluted to nearly 100 ml. A solution of titanium sulphate of known strength is slowly added to the standard from a burette until the colours match. The standard is then diluted exactly to the mark, and the colours again matched.

Standard titanium solution: 0·1000 g. of pure titania is fused with 3 g. of potassium bisulphate. The melt is dissolved in 100 ml. of N. sulphuric acid, and the solution is diluted to one litre. 1 ml. = 0·0001 g. $TiO_2$.

The pure titania is conveniently prepared by fusion of about 0·25 g. of finely powdered rutile with 3 g. of potassium bisulphate, solution of the melt in 50 ml. of ammonium oxalate solution, and filtration. The filtrate is diluted to 150 ml.; 100 ml. of saturated ammonium chloride solution is added, and the boiling liquid is stirred and treated with a freshly prepared 5 per cent. solution of 3 g. of tannin. The red precipitate is collected on an ashless 12·5-cm. filter under slight suction, returned to the beaker with 200 ml. of hot 2 per cent. ammonium chloride solution, thoroughly stirred, again collected, and washed. After strong ignition, it is lixiviated with hot hydrochloric acid (1 : 2 water), again collected, washed with dilute hydrochloric acid, and ignited.

A number of other reagents giving strongly coloured titanium compounds have been proposed for the colorimetric determination of the element, but they do not appear to possess any marked advantages over hydrogen peroxide, and have not come into general use.[2]

§ **VII. Detection in Minerals.**—(*a*) The fine powder is fused with 10 parts of sodium carbonate (with addition of a little nitrate if necessary), the cold melt is extracted with hot water (elimination of chromate, vanadate, molybdate, phosphate), and the insoluble matter is allowed to settle. The clear liquid is decanted off and the residue collected, washed with hot water, ignited in a silica crucible, and fused with bisulphate. The melt is dissolved in 5 per cent. sulphuric acid, the filtered solution affording the following reactions:

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[1] *Ber.*, 1882, **15**, 2599.

[2] Thymol: Lenher and Crawford, *J. Amer. Chem. Soc.*, 1913, **35**, 138; salicylic acid: Jorissen, *Bull. Acad. roy. Belg.*, 1903, p. 902; dihydroxymaleic acid: Fenton, *J. Chem. Soc.*, 1908, **93**, 1064.

(1) Hydrogen peroxide gives an intense orange-brown colour if much titanium is present, yellow to orange if the amount is small (distinction from tantalum and niobium).

(2) Reduction with zinc and hydrochloric acid gives a violet to mauve solution with considerable titanium.

(3) Sodium salicylate gives an intense orange to yellow colour in the neutralized solution, and no precipitate even on boiling (distinction from zirconium, thorium, tantalum, and niobium). Iron, if present, interferes by giving a violet colour.

(*b*) If a mineral is known or suspected to contain tantalum and niobium, the fine powder is fused with bisulphate, and the cooled melt is extracted with a hot, freshly made 1 per cent. tannin solution in 5 per cent. sulphuric acid.[1] The insoluble residue, containing the earth acids as insoluble, coloured tannin complexes, is filtered off; the filtrate is boiled and treated with 3 g. of oxalic acid, 10 g. of ammonium chloride, and 1 g. of tannin in concentrated solution. The boiling solution is stirred and cautiously neutralized with dilute ammonia; while it is still slightly acid, a bright red flocculent precipitate forms if titania is present.

§ **VIII. Determination in Minerals.**—At the present time, rutile and ilmenite constitute titanium ores of considerable commercial importance. The titania content of these minerals is determined by a gravimetric or volumetric method. Small amounts of titanium (in iron ores, rocks, etc.) are determined colorimetrically.

(*a*) *Gravimetric Determination in Rutile and Ilmenite.*—(1) *Authors' tannin method.*[2] 0·25 g. of finely powdered ore is fused with 3 g. of potassium bisulphate in a silica crucible, the mass being heated until crystals of neutral potassium sulphate separate at the surface of the fluid melt. The cold crucible is filled with saturated ammonium oxalate solution and gently warmed to detach the melt. The contents of the crucible are then transferred with hot water to a 250-ml. beaker, more oxalate solution is added (75 ml. in all), and the beaker is gently heated until everything soluble has dissolved. The solution is filtered into a 600-ml. beaker, the filter being washed with hot water.

*Major titania fraction.* The filtrate (150 ml.) is diluted with an equal volume of saturated ammonium chloride solution, boiled, and precipitated with a concentrated freshly prepared solution of 3 g. of tannin, added drop by drop during brisk agitation. Boiling is continued for one minute, and the voluminous red precipitate, $P^1$, collected under slight suction on a 12·5-cm. No. 40 Whatman filter containing some creamed filter-fibre. The filtrate is poured into an 800-ml. beaker and boiled down, while the precipitate is returned to the beaker with a jet of hot 2 per cent. ammonium chloride wash-liquor (150 ml.); after addition of 1 to 2 drops of hydrochloric acid, the suspension is well churned with the glass rod until the clots are quite broken up, returned to the same paper, the beaker is cleaned with the aid of filter-pulp, and the washing completed. The precipitate is compressed by stronger suction, the filter transferred to a tared porcelain crucible, and heated on an asbestos mat until well charred; ignition is then completed on a triangle, and the resulting $TiO_2$ reserved.

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[1] W. R. Schoeller, *Analyst*, 1929, **54**, 453; *Zeitsch. anal. Chem.*, 1934, **96**, 252; *Analyst*, 1934, **59**, 367.

[2] A. R. Powell and W. R. Schoeller, *Analyst*, 1930, **55**, 605.

*Minor titania fraction.* The washings of $P^1$ are added to the concentrated filtrate, which is treated while boiling with a solution of tannin (1 g.), followed by dropwise addition of N. ammonia, with intervening stirring. Each drop of ammonia produces a transient darkening of the red suspension at the point of incidence, due to the action of tannin on the ferric salt, until the liquid assumes a slight, permanent mauve tint, resulting in a slight discoloration of the red colour. The precipitate, $P^{1a}$, is left to settle and collected as was $P^1$, and ignited separately; if not perfectly white after ignition, it must be fused with bisulphate and retreated by the same process for the removal of the small amount of coprecipitated iron.

The filtrate from $P^{1a}$ is normally free from titania, but should always be tested for complete precipitation as follows: It is boiled and treated with N. ammonia until incipient iron precipitation is indicated by a violet cloudiness. This is just cleared by cautious addition of N. hydrochloric acid to the boiling solution. If no orange flocks are visible, then all the titania has been recovered in $P^{1a}$; otherwise, the small precipitate is collected and added to the bulk.

The ignited titania fractions are cautiously transferred to a 150-ml. beaker and digested for half an hour on a hot-plate with 25 ml. of hydrochloric acid (1 : 2 water). The liquid is made ammoniacal, the oxide collected on an ashless 9-cm. filter, washed with 2 per cent. ammonium chloride solution, and ignited in the tared crucible used for $P^1$. It is weighed, and a deduction made for the ash of 3 (or 4) filters.

The titania thus obtained is pure, the precipitation in two fractions ensuring the recovery of the bulk in the form of $P^1$, which does not require retreatment.

(2) *Cupferron method* (*W. M. Thornton, Jr.*[1]).—0·5 g. of ore is fused with 7 g. of potassium pyrosulphate in a platinum crucible. The melt is dissolved in 35 ml. of sulphuric acid (1 : 1) and a little water in a platinum dish, and the liquid is evaporated to fumes of sulphuric acid. The cooled mass is treated with 50 ml. of water and warmed, and the solution is filtered from silica, which is washed, ignited, volatilized with hydrofluoric and sulphuric acids, and the small residue again fused with a little pyrosulphate. The solution of this melt is added to the main portion, which is then made up to 250 ml.

A portion of 100 ml. (equivalent to 0·2 g. of ore) is treated with 2 g. of citric acid, neutralized with ammonia, and re-acidified with 2·5 ml. of 1 : 1 sulphuric acid. The solution is saturated with hydrogen sulphide, and the small precipitate of platinum sulphide filtered off and washed; the filtrate is made ammoniacal, and the iron is precipitated as sulphide by further treatment with hydrogen sulphide. The precipitate is left to settle, collected on close-textured paper, and washed with dilute ammonium sulphide wash-liquor. The filtrate is acidified with 40 ml. of sulphuric acid (1 : 1), boiled until hydrogen sulphide is expelled, cooled, and the titanium is precipitated by cupferron as described in § III, *e*.

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[1] *Titanium*, New York, 1927, p. 161.

Although Thornton states that he " has never failed to find both chromium and vanadium in all specimens of rutile and ilmenite thus far examined," he gives no directions for determining the vanadic oxide in the ignited cupferron precipitate. The vanadium is quantitatively precipitated with the titania, and its presence in the ignited precipitate is indicated by a more or less decided greyish tint, as against the pure creamy-white appearance of the ignited tannin precipitate (*a*, 1, *above*). As the vanadic oxide in rutile may amount to several tenths of one per cent., it is necessary to subject the cupferron precipitate to further manipulation. We fuse the titania with sodium carbonate in a platinum crucible and extract the melt with hot water (§ III, *f*). The purified titania may be determined direct (after treatment with dilute acid, then ammonia), or the vanadium in the alkaline filtrate may be determined by acidification with acetic acid, boiling, and precipitation with tannin. The blue-black precipitate is collected, washed, and ignited; the residual $V_2O_5$ is weighed, and its weight deducted from that of the crude titania.

(*b*) *Volumetric Determination in Rutile and Ilmenite.*—The following method is generally used in the United States for the evaluation of ilmenite: 0·5 g. of the finely crushed ore (or 0·4 g. of rutile) is fused for half an hour in a 250-ml. conical flask with 20 g. of potassium bisulphate. When solution is complete, the flask is manipulated so that the melt spreads round the sides and bottom of the flask. When cool, the melt is dissolved in 100 ml. of 1 : 1 hydrochloric acid, treated with 60 g. of mossy amalgamated zinc, and heated to gentle boiling. It is then poured through a Jones reductor containing a column (13 cm. by 3 cm.) of washed 20-mesh amalgamated zinc covered with 10 per cent. hydrochloric acid. The reductor carries a tap at the lower end, and is inserted in a doubly perforated rubber stopper, the other perforation holding a glass tube for admission of carbon dioxide into the receiver. An atmosphere of carbon dioxide is maintained in the receiver, the gas escaping through a small side slit in the stopper. The passage of the solution through the reductor should occupy 3 to 5 minutes; the reductor is then washed with 10 per cent. hydrochloric acid, care being taken to keep the zinc column covered with liquid.

When the washing of the reductor is concluded, 20 ml. of saturated potassium thiocyanate solution is added to the liquid in the receiver, and the solution is at once titrated with 0·1N. ferric alum solution to a straw-coloured tint.

The ferric alum solution (48 g. per litre of 1 per cent. sulphuric acid) is standardized by being run through the Jones reductor, and titrated with permanganate solution standardized against sodium oxalate. A solution of titanic sulphate standardized at the same time as the ferric alum solution is used as a control with each batch of samples.

It should be observed that the procedure makes no provision for the presence of small quantities of chromium and vanadium in the ore. Both elements are reduced to the bivalent state by zinc, and re-oxidized by ferric salt.

(*c*) *Colorimetric Determination of Small Quantities in Iron Ores.*—Many titaniferous magnetites carry considerable amounts of titania, being intermediate in composition between magnetite and ilmenite; the determination of titania in such ores is carried out gravimetrically (*above*), 0·5 g. being taken.

(1) For the rapid approximate determination of small amounts of titania in other iron ores, 0·5 to 1 g. is fused with potassium bisulphate, and the melt is dissolved in 10 per cent. sulphuric acid. The filtered solution is treated with phosphoric acid and hydrogen peroxide as described in § VI, and the colour is matched against that of a standard prepared under the same conditions as the assay. The insoluble residue from the bisulphate fusion may still contain a trace of titania, while, on the other hand, a little vanadium in the ore may tend to produce a high result.

(2) The accurate determination of minute quantities involves separation of titanium from iron, and vanadium if present. The ore (1 to 2 g.) is decomposed with hydrochloric acid, with or without nitric acid, and the acid liquor is evaporated with 20 ml. of 1 : 1 sulphuric acid until heavy white fumes appear. The cooled mass is diluted with water, heated, and the solution is filtered. The residue is ignited in a platinum crucible, and heated with hydrofluoric and sulphuric acids until the acids are expelled. The crucible, *p*, is reserved.

The filtrate is diluted to 100 ml. and treated with hydrogen sulphide; a small amount of copper sulphate (0·01 g. Cu) may be added to promote flocculation. The precipitate is left to settle, filtered off, and washed with 10 per cent. sulphuric acid containing hydrogen sulphide. The filtrate is caught in a 500-ml. conical flask and boiled until hydrogen sulphide is completely expelled. It is rapidly cooled under the tap, and treated with excess of cupferron solution, which precipitates titania and any ferric, but not ferrous, iron (§ III, *e*). The precipitate is collected with the help of moderate suction, washed with N. hydrochloric acid, and ignited in crucible *p* containing the insoluble residue.

The ignited precipitate is fused with sodium carbonate, the cold melt is extracted with hot water, and the insoluble residue collected and washed with water. It is returned to the crucible, ignited, and fused with bisulphate. The solution of the melt in sulphuric acid is treated with hydrogen peroxide, and the titania determined colorimetrically (§ VI). If a little ferric iron has been coprecipitated by cupferron, a small addition of phosphoric acid is made to assay and standard.

(*d*) *Colorimetric Determination in Rocks.*[1]—(1) One g. of rock powder is heated in a platinum basin with a mixture of hydrofluoric and 1 : 1 sulphuric acids. When decomposition is complete, the liquid is heated until the sulphuric acid fumes strongly. After cooling, more dilute sulphuric acid is added, and the fuming is repeated. Four or five repetitions of this procedure are required to make sure that every trace of fluorine is expelled, otherwise the titania result will be too low. The excess of sulphuric acid over 10 ml. is evaporated off, the residual acid is diluted with water, and the cold solution or an aliquot portion is tested colorimetrically.

[1] H. S. Washington, *The Chemical Analysis of Rocks*, New York, 1930, p. 189.

(2) *Hillebrand's method.*[1] One g. of rock powder is fused with 10 g. of sodium carbonate for half an hour over a blast-burner. The cold melt is extracted with boiling water; the insoluble residue is filtered off, washed with 2 per cent. sodium carbonate solution, ignited, and fused with potassium bisulphate. The melt is dissolved in 10 per cent. sulphuric acid, the solution diluted to 250 ml., and an aliquot portion tested colorimetrically after addition of 5 ml. of phosphoric acid. The standard is made up with the same quantities of reagents as the aliquot portion.

(*e*) *Gravimetric Method for Bauxite.*[2]—The powdered ore (0·5 g.) is treated in a platinum dish with 10 ml. of water, 5 ml. of sulphuric, 5 ml. of nitric, and 5 to 10 ml. of hydrofluoric, acid. The covered dish is heated, first on the water-bath for half an hour with occasional stirring, then more strongly until heavy fumes are evolved. The dish is cooled, rinsed down with water, which is stirred into the acid mass, and the fuming repeated. The cold residue is treated with 50 ml. of warm water, and the soluble salts are dissolved by heating. If a slight residue remains, it is mixed with filter-pulp, collected (the filtrate, F, is reserved), washed with hot water, ignited in a platinum crucible, and fused with a little sodium carbonate. The melt is dissolved in dilute sulphuric acid, and if silica is suspected to be present, the solution is treated with hydrofluoric acid and evaporated until the sulphuric acid fumes. After dilution, the evaporation is repeated. The residue is dissolved in warm water, and the solution is added to the main filtrate F.

The titania in the combined filtrates is determined by the tannin method (§ III, *d*).

(*f*) *Determination in Ferrotitanium.*—0·5 g. of the finely divided material is dissolved in dilute *aqua regia*, and the solution is evaporated with 20 ml. of 1 : 1 sulphuric acid until heavy white fumes are evolved. After cooling, the acid is gradually diluted with water, and the assay digested with a little hydrochloric acid till clear. The insoluble fraction is collected, ignited, and evaporated with hydrofluoric and sulphuric acids; the fixed residue is fused with bisulphate, and the solution of the melt in dilute sulphuric acid is added to the main filtrate, which is treated for the determination of titania as described in § VIII, *a*.

**§ IX. Complete Analysis of Rutile and Ilmenite.**—(*a*) *First Portion*, 0·25 g.—For titania and total iron. See § VIII, *a*, 2.

(*b*) *Second Portion*, 0·5 g.—For silica, manganese, calcium, magnesium, chromium, vanadium, aluminium, zirconium. The ore is fused with bisulphate, and the melt dissolved as under (*a*); the residue is collected, washed, ignited in a platinum crucible, and fused with sodium carbonate, etc. for the determination of silica by the usual method, the filtrate from the silica being added to that from the bisulphate melt.

The cold solution is treated with 5 g. of ammonium chloride and slight excess of ammonia, the precipitate filtered off after short standing, and washed twice with 2 per cent. ammonium nitrate solution; it is then returned to the beaker, dissolved in 25 ml. of 1 : 1 hydrochloric acid, and the precipitation with ammonium chloride and ammonia repeated. The precipitate is mixed with filter-pulp, again collected, washed, and ignited in a platinum crucible.

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[1] W. F. Hillebrand, *Bull.* **422,** *U.S. Geol. Surv.*, p. 136.

[2] Solution procedure of Hillebrand and Lundell, *op. cit.*, p. 868.

The combined filtrates are slightly acidified, boiled down to 150 ml., and used for the determination of manganese, calcium, and magnesium.

The ignited ammonia precipitate is fused for an hour with 5 g. of sodium carbonate, the melt extracted with hot water in a porcelain dish, and the extract filtered; the residue is washed with 2 per cent. sodium carbonate solution, returned to the dish, and treated with dilute hydrochloric acid. The suspension is treated with a slight excess of ammonia, collected on the same filter, washed with ammonium nitrate solution, and ignited in the platinum crucible. The carbonate fusion, extraction with hot water, and filtration are repeated, the two extracts being combined, slightly acidified with hydrochloric acid, and boiled down to 100 ml. after addition of sulphurous acid to reduce chromate and vanadate.

The concentrated solution is treated with 10 g. of ammonium acetate, and precipitated while boiling with a solution of 0·5 g. of tannin. The flocculent precipitate is allowed to settle on a hot-plate, collected, washed with ammonium nitrate solution, ignited in a tared platinum crucible, and weighed as ($Cr_2O_3 + V_2O_5 + Al_2O_3$). The mixture of oxides is fused with a little potassium carbonate, the melt is dissolved in water, and the yellow tint of the solution matched against that of a standard solution of potassium chromate. The solution is then acidified with sulphuric acid, precipitated with cupferron, and the precipitate ignited to $V_2O_5$, which is weighed (**XVII**, § IV, *b*). Alumina is found by difference.

The insoluble titania residue from the double sodium-carbonate fusion is fused with bisulphate, the melt dissolved in 10 per cent. sulphuric acid, and the solution tested for zirconia with hydrogen peroxide and ammonium phosphate (**XIV**, § VI, *d*).

(*c*) *Third Portion.*—For sulphur. 1 g. is fused with sodium carbonate and potassium nitrate. The melt is extracted with water, and the filtered extract is analysed for sulphate by the usual method.

(*d*) *Fourth Portion.*—For phosphorus. 1 g. is fused with sodium carbonate and potassium nitrate, the melt extracted with water, and the filtered extract evaporated to dryness with excess of nitric acid. The residue is baked at 130° C., dissolved in dilute nitric acid, the solution filtered, and the filtrate precipitated with ammonium nitrate and molybdate mixture.

(*e*) *Fifth Portion.*—For ferrous oxide. 0·5 g. of the finely ground mineral is placed in a large platinum crucible provided with a perforated lid carrying a platinum tube, and treated with 10 ml. of 1 : 1 sulphuric and 20 ml. of strong hydrofluoric acids. A current of carbon dioxide (or nitrogen) is passed through the tube into the crucible to displace air, after which the crucible is gently heated below boiling temperature for 20 to 30 minutes. After cooling to 50° C. under carbon dioxide, the contents of the crucible are poured into 500 ml. of cold saturated boric acid solution containing 10 ml. of sulphuric acid. The ferrous iron in the solution is titrated with 0·1N. permanganate standardized against sodium oxalate.

(*f*) *Sixth Portion.*—Tin in rutile. Tin is sometimes found in minute quantities in rutile. 1 g. of finely powdered mineral is fused with 6 g. of potassium bisulphate in a silica crucible, the melt is dissolved in a hot solution of 6 g. of tartaric acid in 100 ml. of 5 per cent. sulphuric acid, and the unfiltered liquid is treated with hydrogen sulphide till cold. The small precipitate is left to settle overnight, collected, washed with hydrogen-sulphide water containing a few drops of sulphuric acid, cautiously ignited in porcelain, and transferred to a nickel crucible. After fusion of the residue with a little sodium peroxide, the tin is determined by reduction with iron and titration with dilute iodine solution as usual.

(*g*) *Combined water*, if present, is determined by Penfield's method.

## XIV.—ZIRCONIUM AND HAFNIUM.

§ I. **Minerals.**—Hafnium invariably accompanies zirconium in its minerals, the oxide $HfO_2$ replacing an equivalent amount of $ZrO_2$. According to von Hevesy, the discoverer of hafnium, the average atomic ratio Zr : Hf in minerals is 100 : 1.[1] In the list of minerals given *below*, the terms "zirconium" and "zirconia" refer to mixtures of the two elements or the two oxides in their natural proportions.

(*a*) *Oxides.*—(1) *Baddeleyite*, zirconium dioxide, occurs as monoclinic tables often twinned. They have a greasy to vitreous lustre and a nearly perfect cleavage. The colour varies according to the percentage of iron, from white, through yellow, brown, and red, to black. H. 6; sp. gr. 5·7.

(2) *Brazilian zirconia rock*, *brazilite*, *caldasite*, is a compact, hard, intimate mixture of amorphous baddeleyite, zircon, ferric oxide, aluminium silicate, and titania in variable proportions. Dark to light grey; brownish-white to red-brown if ferruginous. The sp. gr. increases with the zirconia content from about 4·2 (60 per cent.) to 4·9 (80 per cent. $ZrO_2$). Also found in the form of water-worn pebbles ("favas"). The most abundant source of zirconium.

(3) *Zirkelite* is a complex mixture of iron oxide, lime, zirconia, titania, and thoria. Brittle, resinous, black octahedra having a conchoidal fracture. H. 5·5; sp. gr. 4.

(4) *Uhligite*, a complex mineral found in bright black octahedra; a mixture of lime, alumina, titania, and zirconia.

(*b*) *Silicates.*—(1) *Zircon*, zirconium orthosilicate, $ZrSiO_4$, is found in brittle tetragonal prisms isomorphous with rutile, thorite, and cassiterite. Colour variable: it has been found colourless, red, brown, green, yellow, and black. Lustre adamantine, double refraction strong. No cleavage. H. 7·5; sp. gr. 4·7. Zircon is a minor constituent of some igneous rocks and pegmatites, the disintegration of which yields detrital deposits, from which large quantities of zircon are obtained.

(2) *Naegite*, a radioactive variety of the above, contains yttrium, thorium, and tantalum.

(3) *Lavenite*, a complex silicate of iron, manganese, and zirconium containing tantalum. Yellow to brown monoclinic tables, with vitreous lustre and perfect cleavage. H. 6; sp. gr. 3·5.

(4) *Hainite*, a complex silicate of calcium, sodium, titanium, and

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[1] G. von Hevesy and R. Hobbie, *Zeitsch. anorg. Chem.*, 1933, **212**, 142.

zirconium containing tantalum. Pale yellow triclinic needles or plates with vitreous lustre.

(5) *Eudialyte*, a silicate of zirconium, sodium, calcium, and iron containing chlorine. Red to brown translucent rhombohedral tables. Lustre resinous. H. 5·5; sp. gr. 2·9.

(6) *Rosenbuschite*, a silicate and fluoride of zirconium, titanium, sodium, and lime. Orange, vitreous, monoclinic crystals. H. 5·5; sp. gr. 3·3.

§ **II. Properties and Compounds.**—(*a*) *Zirconium.*—(1) The *metal* is obtained by reduction of potassium fluorozirconate with sodium in presence of sodium chloride. The fused metal is white, hard (H. 7 to 8), and brittle; sp. gr. 6·52; m.p. 2130° C. It is very resistant to acids, being attacked only by *aqua regia* and by hydrofluoric acid. When heated, it combines with oxygen (to $ZrO_2$), nitrogen (to $Zr_3N_2$), and hydrogen (to $ZrH_2$).

(2) The *dioxide*, $ZrO_2$ (zirconia), is a dense white powder, remaining white when heated, and very resistant to acids and alkalis. Soluble in molten pyrosulphate, but remains insoluble after fusion with alkali carbonate. It is used as a refractory on account of its inertness and high melting-point (about 2700° C.); it volatilizes at 3000° C. Sp. gr. 5·73. Obtained by ignition of the nitrate, oxalate, hydroxide, or oxychloride.

(3) The *hydroxide* is precipitated by ammonia or caustic alkali from zirconium solutions. It is white, gelatinous, insoluble in excess of the precipitant, and contains an indefinite amount of water. When precipitated in the cold, it is soluble in dilute acids; but if thrown down from hot solutions, or after contact with hot water, it is soluble only in strong acids.

(4) *Zirconyl chloride*, $ZrOCl_2.8H_2O$ (zirconium oxychloride), is formed when the hydroxide is dissolved in hydrochloric acid. It is readily soluble in water, but slightly so in hydrochloric acid, from a solution of which it crystallizes in tetragonal prisms.

(5) The *fluoride*, $ZrF_4.3H_2O$, is soluble in water containing free hydrofluoric acid (difference from thorium). The addition of potassium fluoride to the solution causes deposition of crystals of potassium fluorozirconate, $K_2ZrF_6$, which is soluble in 70 parts of cold and 4 parts of boiling water.

(6) *Zirconyl oxalate* is a white powder formed when the requisite quantities of solutions of a zirconium salt and a soluble oxalate are mixed. Soluble in ammonium oxalate or oxalic acid solution.

(7) *Zirconium sulphate*, $Zr(SO_4)_2.4H_2O$, is obtained by solution of the hydroxide in sulphuric acid. Potassium sulphate gradually precipitates potassium zirconyl sulphate from the cold solution.

(8) *Zirconium phosphate*, $Zr(HPO_4)_2$, is a white flocculent precipitate produced in zirconium solutions by soluble phosphates; it is insoluble even in fairly strong acids (*e.g.* 20 per cent. sulphuric acid by weight), and on ignition is converted into the pyrophosphate, $ZrP_2O_7$.

(*b*) *Hafnium.*—Hafnium bears the closest resemblance to zirconium in all its chemical properties and compounds. It is more basic than zirconium; some of its salts (*e.g.* potassium fluorohafniate) are slightly more soluble than those of zirconium, whilst its phosphate is even more insoluble in acids than the zirconium precipitate.

The *element* has a sp. gr. of 13·31, and melts at 2500° C.; *hafnium dioxide* (hafnia), sp. gr. 9·67, is obtained by ignition of the hydroxide (gelatinous white precipitate), sulphate, nitrate, oxalate, or hafnyl chloride.[1]

*Note.*—Throughout the remaining paragraphs of the present section, the terms " zirconium " and " zirconia," used without qualification, refer to a mixture of zirconium and hafnium, or zirconia and hafnia, in the proportions usually encountered in minerals, *viz.* about 99 per cent. of the former to 1 per cent. of the latter.

The only exception to this rule will be found under § III, *m*, where the processes aiming at a separation of these two closely related elements are discussed.

§ **III. Quantitative Separation.**—Whilst the discovery of hafnium as a constant minor mineral associate of the element zirconium has created a separation problem almost as difficult as those presented by the rare-earth group, the analytical chemistry of zirconium has otherwise been fairly fully explored. We have recently been able to contribute to the knowledge of the subject by quantitatively resolving the quaternary mixture $(Zr,Hf)O_2$, $TiO_2$, $Ta_2O_5$, $Nb_2O_5$ into its components;[2] in particular, we have shown the striking differences in colour and solubility between the tannin complexes of zirconium and titanium, which form the basis of our method for this more frequent separation case.[3]

The insolubility of zirconium phosphate in mineral acid is a factor of cardinal importance in the analytical chemistry of this element. Recent researches have shown that arsenic acid[4] and some of its derivatives[5] likewise yield highly insoluble zirconium compounds. The arsenate can be converted into zirconia by ignition under reducing conditions; it is therefore more advantageous than the phosphate, the direct weighing of which presents difficulties, while its conversion into zirconia requires single or double fusion with sodium carbonate. The precipitation of zirconium as basic selenite[6] from mineral acid solution is a useful alternative to cupferron precipitation; upon ignition, the selenite is converted into zirconia.

(*a*) *From Metals of the Hydrogen-sulphide Group.*—Zirconium is not precipitated as sulphide from acid solution, and its sulphate is much less prone to hydrolyse than titanium sulphate (*cf.* **XIII,** § III, *a*).

(*b*) *From Iron, Zinc, Nickel, Cobalt, Manganese.*—(1) *Ammonium sulphide method;* (2) *Thiosulphate method;* (3) *Ether extraction for large quantities of iron*: As for titanium (see **XIII,** § III, *c*).

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[1] For the discovery, occurrence, and properties of hafnium, see G. von Hevesy, *Chemical Analysis by X-Rays and its Applications*, New York, 1932, pp. 177–252.

[2] W. R. Schoeller and E. F. Waterhouse, *Analyst*, 1928, **53**, 515; W. R. Schoeller, *ibid.*, 1929, **54**, 453; W. R. Schoeller and A. R. Powell, *ibid.*, 1932, **57**, 550.

[3] A. R. Powell and W. R. Schoeller, *ibid.*, 1930, **55**, 605.

[4] L. Moser and R. Lessnig, *Monatsh.*, 1924, **45**, 323; W. C. Schumb and E. J. Nolan, *Ind. Eng. Chem.*, *Anal. Ed.*, 1937, **9**, 371.

[5] Phenylarsonic acid: A. C. Rice, H. C. Fogg, and C. James, *J. Amer. Chem. Soc.*, 1926, **48**, 895; *n*-propylarsonic acid: H. H. Geist and G. C. Chandlee, *Ind. Eng. Chem.*, *Anal. Ed.*, 1937, **9**, 169; methylarsinic acid: R. Chandelle, *Bull. Soc. chim. Belg.*, 1937, **46**, 283.

[6] M. M. Smith and C. James, *J. Amer. Chem. Soc.*, 1920, **42**, 1764; S. G. Simpson and W. C. Schumb, *ibid.*, 1931, **53**, 921.

(*c*) *From Titanium, Niobium, Tantalum.*—(1) *Authors' tannin method.* The action of tannin as a group reagent in precipitating tantalum, titanium, and niobium (Group A) has been explained in **XIII,** § III, and working directions have been given thereunder (§ III, *d*).

Zirconium, being a member of Tannin Group B, passes into the filtrate or filtrates from the Group A precipitate. If the absolute amount of zirconia is less than 0·1 g., the filtrate is evaporated to 500 ml. and precipitated while boiling with 1 g. of tannin and a slight excess of ammonia. The precipitate is left to settle at 60° to 70° C. for an hour, collected under gentle suction, returned to the beaker, and stirred up with dilute ammonium nitrate solution, again collected, washed, and ignited to $(Zr,Hf)O_2$. It may require lixiviation, and should be tested for silica by fusion with bisulphate, solution of the melt in dilute sulphuric acid, filtration, and ignition of the small insoluble residue.

If the quantity of zirconia in the filtrate from Group A is more substantial, the ammonium salts and the tannin in the solution are destroyed by evaporation with 50 ml. of nitric and 10 ml. of sulphuric acid until white fumes are evolved. After cooling, the acid is diluted with 100 ml. of water, the solution filtered, and the zirconium precipitated with ammonia (§ IV, *a*—see **XIII,** § IV, *a*).

(2) *Pyrosulphate-tannin method.*—See **XVIII,** § III, *h*, 1.

(*d*) *From Niobium and Tantalum.*—If a small quantity of zirconia is to be separated from large amounts of earth acid, the tannin precipitate produced by the method described under (*c*), *above*, becomes inconveniently large. In such cases a combination process involving fusion with potassium carbonate as the first step is preferable.[1]

The mixed oxides are fused with 6 parts of potassium carbonate in platinum, and the cold melt is extracted with hot water containing less than 0·5 g. of potassium hydroxide. The turbid liquid is transferred to a 250-ml. beaker, treated with a little filter-pulp to entangle the finely divided zirconia, and filtered through close-textured paper containing a pad of filter-pulp pressed into the apex. The filtrate should again be passed through the same filter if necessary. The insoluble residue is washed with 2 per cent. potassium carbonate solution, and the filter returned to the beaker and stirred to a pulp; the liquid is acidified with hot dilute hydrochloric acid, then made slightly ammoniacal. The precipitate is left to settle for a short time on a hot-plate, collected, washed with 2 per cent. ammonium nitrate solution, and ignited in a silica crucible. The precipitate contains the whole of the zirconia together with a small amount of earth acid; it is fused with bisulphate, the melt dissolved in ammonium oxalate, and the separation is completed by the tannin process (*c*, *above*).

In the potassium carbonate fusion part of any titania present remains in the zirconia residue; the balance goes into solution with the earth acids, especially if niobium preponderates over tantalum.[2]

(*e*) *From Titanium, Aluminium, Iron, and All Metals having Soluble*

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[1] W. R. Schoeller and E. F. Waterhouse, *Analyst*, 1928, **53**, 515; W. B. Giles, *Chem. News*, 1909, **99**, 1.

[2] W. R. Schoeller and E. C. Deering, *Analyst*, 1927, **52**, 631.

*Sulphates.*—(1) *Phosphate method.*[1] Zirconium is precipitated as phosphate by alkali phosphate from sulphate solutions at an acid concentration at which no other metals, with the exception of titanium, are precipitated; the precipitation of titanium phosphate can be prevented by addition of hydrogen peroxide, which converts titanium compounds into pertitanic acid.

The phosphate reaction is, therefore, characteristic of zirconium; at the same time, it is very sensitive, since a fraction of a mg. of zirconia yields a bulky, flocculent, colourless precipitate.

The disadvantage of zirconium phosphate from the point of view of gravimetric work is its variable and uncertain composition, which has led to the use of factors ranging from 36 to over 50 per cent. of $ZrO_2$. Whilst, therefore, phosphate precipitates not exceeding a few mg. in weight may be weighed as such, it is necessary to convert larger quantities into zirconia at the cost of further manipulation. Hence the application of the phosphate process is confined to materials very low in zirconia (*e.g.* rocks).

The sulphate solution is treated with one-tenth its volume of strong sulphuric acid, an excess of pure hydrogen peroxide if titania is present, and a large excess of freshly prepared 10 per cent. diammonium phosphate solution over that required for the compound $Zr(HPO_4)_2$: a hundredfold excess is prescribed for a few mg., a tenfold excess for more substantial amounts. The solution is kept at 50° C. for a few hours; small precipitates are set aside overnight. The precipitate is mixed with filter-pulp, collected, thoroughly washed with cold 5 per cent. ammonium nitrate solution, dried in a platinum crucible, and ignited very gently until the charred mass has been entirely oxidized. With substantial amounts of zirconia this is a very tedious process. The ignition is completed over a blast-burner. The $ZrO_2$ factor recommended by Lundell and Knowles is 0·4632.

For accurate work the precipitate, if at all large, should be fused with sodium carbonate, the melt extracted with hot water, and the washed residue ignited and fused with bisulphate. The resultant solution in dilute sulphuric acid is precipitated with ammonia, and the precipitate ignited to $(Zr,Hf)O_2$ (§ IV, *a*—see **XIII**, § IV, *a*). As the oxide is liable to retain a little phosphate, it may be advisable to repeat the whole cycle of operations beginning with the sodium carbonate fusion.

(2) *Arsenate method.*[2] Zirconium is quantitatively precipitated by diammonium arsenate from 2·5N. hydrochloric or 3·75N. nitric acid solution; if thorium, cerium, and titanium accompany the zirconium, double precipitation should be employed, and the weighed zirconia tested colorimetrically for titania. The application of this method to ore analysis is described under § VI, *b*, *below*.

(3) *From titanium only.* (*a*) *Zirconia preponderates.* The titania is determined gravimetrically by the tannin method (*c*, *above*), or colorimetrically if only a few mg. are present (**XIII**, § VI); zirconia by difference.

($\beta$) *Titania largely preponderates.* The zirconia (if below 0·01 g.) is determined gravimetrically by the phosphate method (*above*); titania by difference.

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[1] W. F. Hillebrand, *Bull.* **176**, *U.S. Geol. Surv.*, p. 75; G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1919, **41**, 1801; P. Nicolardot and A. Réglade, *Compt. rend.*, 1919, **168**, 348.

[2] W. C. Schumb and E. J. Nolan, *Ind. Eng. Chem.*, *Anal. Ed.*, 1937, **9**, 371.

(*f*) *From Aluminium, Uranium, Chromium, Beryllium, Manganese, Nickel, Cobalt, Zinc: Cupferron Method.*[1]—Zirconium is precipitated by cupferron under the same conditions as titanium; the directions given under **XIII,** § III, *e* apply equally to zirconium, except that the reagent does not separate it from small to moderate amounts of phosphoric acid as it does titanium. While the titanium compound of cupferron is yellow, the zirconium compound is white.

(*g*) *From Aluminium.*—(1) *Aluminium preponderates.* The mixed oxides are fused with 30 times their weight of sodium carbonate; the aqueous extract of the melt is digested with a little caustic soda, and filtered. The alumina passes into the filtrate, while zirconia remains insoluble.[2]

(2) *Zirconia preponderates.* Zirconium is precipitated by cupferron (*f, above*), or as basic selenite (*h, below*).

(*h*) *From Aluminium, Iron, Rare Earths, Manganese, Nickel, Cobalt, Zinc, Copper, Lead, Bismuth: Selenious Acid Method.*[3]—The reagent is a 10 per cent. solution of selenious acid. The recovery of zirconium as basic selenite is complete from less than 0·6N. hydrochloric acid solutions. In presence of sulphuric acid, precipitation is very slow. Alkali chloride and nitrate do not interfere, but sulphate does, causing incomplete precipitation at the above acidity. Quadrivalent elements are precipitated; uranium and vanadic acid are adsorbed, but can be eliminated by reprecipitation, the freshly precipitated zirconium selenite being soluble in 6N. hydrochloric acid. Titanium and cerium are removed by double precipitation in presence of hydrogen peroxide; the only element remaining with the zirconium is thorium, which must be separated as oxalate. The procedure is described under § VI, *c, below.*

(*i*) *From Phosphate, Arsenate, Vanadate, Chromate, Molybdate, Tungstate: Sodium Carbonate Fusion Method.*—The separation is carried out as described under **XIII,** § III, *f*. Unlike titania, zirconia is quantitatively separated from tungstic oxide by fusion with sodium carbonate and extraction of the melt with hot water (*cf.* **XIII,** § III, *g*).

(*j*) *From Silica.*—As for titanium (see **XIII,** § III, *h*).

(*k*) *From Thoria.*—See **XV,** § III.

(*l*) *From Rare Earths.*—See **XII,** § III, *a*.

(*m*) *Separation of Zirconium from Hafnium.*—The discovery of hafnium recalls the resolution of didymium into praseodymium and neodymium, and of the "old" ytterbium into ytterbium and lutecium.

A number of previously unknown arc spectrum lines were first mapped by Urbain[4] in 1911, and assigned by him to a new element, celtium, under which name it was briefly noticed in the first edition of this manual.

Urbain does not appear to have done any further work towards the isolation of the unknown element from the small quantity of uncrystallizable lutecium mother-liquor at his disposal; but in 1923 D. Coster, and G. von Hevesy[1] announced the discovery of hafnium in a number of zirconium minerals. Hafnium was said to show the lines previously measured by Urbain, but this is denied by von Hevesy, who states that Urbain's "celtium" lines were weak lutecium lines which became prominent at the high concentration attained by his fractionation technique.

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[1] W. M. Thornton, Jr., *Titanium*, New York, 1927, pp. 90, 107.

[2] J. D. Ferguson, *Eng. Min. J.*, 1918, **106**, 356, 793.

[3] S. G. Simpson and W. C. Schumb, *J. Amer. Chem. Soc.*, 1931, **53**, 921.

[4] G. Urbain, *Compt. rend.*, 1911, **152**, 141.

(1) The separation of zirconium from hafnium, like that of the rare earths from each other, is a proposition of preparative rather than of analytical chemistry. No accurate separation process is known. Actual separation is achieved by repeated recrystallization of potassium fluorozirconate, the hafnium salt accumulating in the mother-liquors. Another method consists in fractional precipitation of the phosphates[2] or arsenates,[3] the hafnium compound being the less soluble in both cases.

The fractional precipitation of the phosphates is carried out in strong sulphuric acid. The mixed sulphates are dissolved in the strong acid, and the solution is treated with enough phosphoric acid to precipitate about one-fifth of the oxides. One and a half volumes of water are next added gradually with vigorous stirring. After settling overnight, the clear liquor is siphoned off, the remainder diluted with three volumes of water, and the precipitate collected on a filter. The filtrate is added to the siphoned liquid and the mixture evaporated until white fumes are evolved, the treatment of the acid liquor being repeated several times. The precipitates are united and fused with sodium carbonate, the resulting oxides are converted into sulphates, and the fractionation is repeated. Seven consecutive precipitations gave a product containing nearly 90 per cent. of the hafnia from a mixture containing 2 to 3 per cent.

(2) *Indirect determination of zirconium and hafnium.* (*a*) *Selenite method.* The precipitation of zirconium as basic selenite[4] has been investigated by Claassen,[5] who succeeded in converting it into the normal selenite $Zr(SeO_3)_2$, which is crystalline and of stoichiometrically definite composition. This was determined gravimetrically by ignition (1000° C.) of the precipitate previously dried at 120° to 200° C., and volumetrically by iodimetric determination of the selenious acid after solution of the precipitate in sulphuric acid and sodium fluoride. Hafnium behaves like zirconium, yielding a basic selenite convertible into the normal compound. The gravimetric determination of hafnium in the selenite gives a mean positive error of 1 per cent., the volumetric determination an error of 1·4 per cent. The indirect simultaneous determination of the two elements in the mixed selenite precipitate is carried out as follows:

The slightly acid solution of the weighed mixed oxides (maximum: 0·6N. sulphuric or hydrochloric acid, but 0·3N. for small quantities of zirconium; maximum for nitric acid: 0·38N.; volume: 400 ml. for 0·1 g. of zirconium) is precipitated in the cold with 2 g. of selenious acid in 10 per cent. solution, heated to boiling, and set aside for 5 to 20 hours on a steam-bath or hot-plate until the flocculent precipitate has become dense and crystalline. It is collected in a porcelain filtration crucible (G4) for the gravimetric determination, or on a paper filter for the volumetric determination, washed eight times by decantation with hot water (hot dilute hydrochloric acid may be used if other elements are present), then with cold water until the washings give no selenium reaction with starch, potassium iodide, and dilute sulphuric acid. For the gravimetric determination, the crucible and its contents are dried at 120° to 200° C., weighed, and then ignited to constant weight. Zirconium selenite contains 35·70 per cent. of zirconia, hafnium selenite 48·69 per cent. of hafnia. Hence each 0·1299 per cent. over 35·70 represents 1 per cent. of hafnium selenite, or 0·4869 per cent. of hafnia, in the mixed selenites. Or 1 per cent. of oxide over 35·70 represents 3·748 per cent. of hafnia in the mixed selenites.

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[1] G. von Hevesy, *Ber.*, 1923, **56**, 1503.

[2] J. Bardet and C. Toussaint, *Compt. rend.*, 1925, **180**, 1936.

[3] L. Moser and R. Lessnig, *Monatsh.*, 1924, **45**, 327.

[4] S. G. Simpson and W. C. Schumb, *J. Amer. Chem. Soc.*, 1931, **53**, 921; abstract: *Analyst*, 1931, **56**, 337.

[5] A. Claassen, *Zeitsch. anal. Chem.*, 1939, **117**, 252.

The volumetric determination is preferable on account of the greater difference between the two conversion factors: 0·1000 g. of $ZrO_2$ as selenite consumes 64·92 ml. of 0·1N. thiosulphate solution; 0·1000 g. of $HfO_2$ consumes 37·99 ml. The mixed selenite precipitate is rinsed off the filter with a little water and dissolved by gentle heating with 6 ml. of sulphuric acid (1 : 1) and 10 ml. of 3 per cent. sodium fluoride solution; the warm solution is filtered through the same paper into a 750-ml. conical flask, and the paper is washed with a little dilute acid containing fluoride. The cold solution is diluted (200 to 300 ml.), treated with 10 to 15 ml. of 2 per cent. starch solution, a little sodium bicarbonate, and a solution of 4 g. of potassium iodide free from iodate, and titrated after 2 minutes with 0·1N. thiosulphate solution. The excess of starch is added for the purpose of keeping the selenium in colloidal solution, thus preventing it from adsorbing iodine. As the titration proceeds, the dark blue solution becomes lighter, then dirty brown; the end-point, a sudden change to pale red, is accurate to one drop, especially if the flask rests on an illuminated pane of opal glass. The volumetric determination gives results reproducible within 0·3 per cent.; the hafnium content in zirconium can be determined within 1 per cent., if an empirical hafnium factor (*i.e.* the theoretical factor multiplied by 1·01) for the thiosulphate solution is used.

(β) *Sulphate method.* A gravimetric method for the indirect determination of zirconia and hafnia in binary mixtures of substantial quantities of the two oxides consists in converting them into the sulphates, which are heated at 400° C. to constant weight. The weighed anhydrous sulphates are then converted into oxides by heating, at first gently, and finally at 1000° C. to constant weight. Since zirconium sulphate contains 43·49 per cent. of zirconia, whilst hafnium sulphate contains 56·81 per cent. of hafnia, each 0·1332 per cent. over 43·49 of oxide in the anhydrous sulphates represents 1 per cent. of hafnium sulphate, equivalent to 0·5681 per cent. of hafnia; or 1 per cent. of oxide in excess of 43·49 indicates 4·265 per cent. of hafnia in the mixed sulphates.

(γ) *Physical methods.* Two physical methods for the determination of hafnia have been published. The first consists in determining the specific gravity of binary mixtures of zirconia and hafnia.[1] The oxides should always be prepared by the same method, *viz.* decomposition of the mixed sulphates by ignition at 1000° C. A pyknometer of known capacity (about 10 ml.) is weighed empty, and again after introduction of 1 to 4 g. of mixed oxides. The pyknometer is filled with water at 15° C. in a vacuum, left for some hours in a thermostat at 20·0° C., and again weighed. The density of the oxides prepared as described was found to be: 5·73 for zirconia and 9·67 for hafnia; hence the percentage of hafnia in the mixed oxides is given by the expression $\frac{d-5{\cdot}73}{0{\cdot}0394}$ ($d$ = density of the mixed oxides).

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[1] G. von Hevesy and V. Berglund, *J. Chem. Soc.*, 1924, **125**, 2372.

The other physical method, which permits the quantitative determination without any chemical treatment, is based on X-ray spectrography.[1] The mineral powder to be tested is mixed with increasing quantities of tantalum (the neighbour of hafnium in the Periodic System) until the intensity of the corresponding tantalum line equals that of the chosen hafnium line (*e.g.* $L\alpha_1$) in the X-ray spectrogram. This gives the proportion of hafnium in the mixture, which is the same as that of the added tantalum.

**§ IV. Gravimetric Determination.**—Zirconium is always determined gravimetrically, quantities of a few mg. being weighed as phosphate (§ III, *e*); larger amounts are weighed in the form of the dioxide, zirconia. This is obtained by ignition of the precipitate obtained either by ammonia, sodium thiosulphate, tannin, cupferron, ammonium arsenate, or selenious acid.

(*a*) *Ammonia.*—As for titanium (see **XIII,** § IV, *a*).

(*b*) *Thiosulphate.*—As for titanium (see **XIII,** § IV, *e*).

(*c*) *Tannin.*—(1) *Precipitation from oxalate solution.*—See § III, *c*, *above.*

(2) *Precipitation from tartrate solution.*—As for titanium (see **XIII,** § IV, *c*).

(*d*) *Cupferron.*—As for titanium (see **XIII,** § III, *e*).

(*e*) *Arsenate.*—See § VI, *b*, *below.*

(*f*) *Selenious Acid.*—See § VI, *c*, *below.*

**§ V. Detection in Minerals.**—The fine powder is fused with potassium carbonate, the melt extracted with hot water and a few pellets of potassium hydroxide, the insoluble matter left to settle, and the clear solution decanted off. The residue is collected, washed, ignited in a silica crucible, and fused with bisulphate. The cold melt is dissolved in warm 10 per cent. sulphuric acid, the solution filtered, and the filtrate treated at 50° C. with excess of hydrogen peroxide and 10 per cent. ammonium phosphate solution (*cf.* § III, *e*, *above*). A white flocculent precipitate depositing after a short time or (in the case of traces) overnight proves zirconium to be present.

If desired, the identity of the precipitate may be confirmed as follows: It is collected, washed, ignited in platinum, and fused with sodium carbonate. The melt is extracted with hot water, the residue filtered off, washed, ignited in a silica crucible (the oxide remaining white on ignition), and fused with bisulphate.

The solution of the melt (filtered if necessary) contains zirconium sulphate. It is treated with an excess of sodium hydroxide: the white flocculent precipitate is insoluble in excess of the precipitant (distinction from aluminium and beryllium).

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[1] D. Coster and G. von Hevesy, *Zeitsch. Elektrochem.*, 1923, **29**, 344; H. Mark, in *Spektroskopische und Radiometrische Analyse*, Leipzig, 1933, p. 255.

The hydroxide precipitate is collected, washed, and dissolved in hydrochloric acid. The chloride solution is not precipitated by hydrofluoric acid; treated with oxalic acid, it gives a precipitate soluble in excess (distinction from thorium and rare earths); with tannin and excess of ammonium acetate the boiling solution gives a white precipitate (distinction from titanium).

The chloride solution may be evaporated to dryness on the water-bath, and the residue dissolved in a minimum of water. The dropwise addition of strong hydrochloric acid produces a bulky precipitate of zirconyl chloride, $ZrOCl_2.8H_2O$. The precipitate dissolves when the solution is heated, and on cooling the salt crystallizes in fine, silky needles.

§ **VI. Determination in Ores.**—(*a*) *In Zircon, Baddeleyite, Brazilian Zirconia Rock, and Oxide and Silicate Minerals High in Zirconia.*—A variety of fluxes has been proposed for the decomposition of minerals high in zirconia. We have not encountered any serious difficulty in decomposing such materials by a sodium carbonate fusion followed by bisulphate treatment of the residue from the carbonate fusion.[1] If the ore to be analysed is ferruginous (*e.g.* reddish-brown Brazilian zirconia rock), it should be extracted with strong hydrochloric acid prior to fusion with soda, so as to avoid the risk of slight reduction to metallic iron, which by alloying would contaminate the platinum crucible.[2] The quantity of zirconia in the assay should not exceed 0·25 g.

0·25 g. of slimed mineral (if ferruginous) is digested with 10 ml. of strong hydrochloric acid. The solution is evaporated to dryness, the residue extracted with 25 ml. of hot N. hydrochloric acid, and the insoluble portion collected, washed, and ignited in a platinum crucible. The filtrate, F, is reserved.

The ignited insoluble residue from the above operation, or the weighed mineral if non-ferruginous, is fused with 5 g. of sodium carbonate over a blast-burner for an hour. The cold melt is disintegrated with boiling water, and the insoluble collected, washed with 2 per cent. sodium carbonate solution and twice with water, ignited, and fused with 4 g. of potassium bisulphate in silica. The cold melt is dissolved in warm 5 per cent. sulphuric acid; the insoluble fraction is filtered off, ignited in platinum, evaporated with hydrofluoric and sulphuric acids, and the residue again fused with bisulphate. The solution of the melt, together with the filtrate F, is added to the main sulphate solution, which is then saturated with hydrogen sulphide, and any precipitate removed by filtration.

The filtrate, which contains iron in the ferrous state, is treated with 4 g. of tartaric acid and a small excess of ammonia, followed by hydrogen sulphide to precipitate the iron as sulphide. Next day the precipitate is filtered off and washed as usual.

The filtrate is treated with 40 to 60 ml. of sulphuric acid (1 : 1), freed from hydrogen sulphide by boiling, cooled to 10° C., and diluted to 400 ml.

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[1] A. R. Powell and W. R. Schoeller, *Analyst*, 1919, **44**, 397; Borax fusion: G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1920, **42**, 1439.

[2] *Cf.* R. B. Sosman and J. C. Hostetter, *J. Amer. Chem. Soc.*, 1916, **38**, 807, 1188.

A cold, freshly prepared and filtered 6 per cent. solution of cupferron is then added in liberal excess during agitation. The precipitate is mixed with filter-pulp, collected without delay under slight suction, returned to the beaker with N. hydrochloric acid, stirred up with 100 ml. of the acid wash-liquor, returned to the filter, washed, and finally compressed as much as possible by strong suction. It is ignited wet in a tared silica crucible, first on an asbestos mat in a fume-chamber and eventually over a blast-burner, and weighed. It includes the whole of the titania present in the ore, and minor quantities of thoria and rare earths, if present. These oxides are next determined and deducted from the weight found, zirconia being taken by difference.

The weighed precipitate is fused with sodium bisulphate, and the melt extracted with 5 per cent. oxalic acid solution.[1] The liquid is transferred to a beaker with the oxalic acid solution (about 100 ml. in all), digested on a steam-bath until the precipitate becomes crystalline, and set aside cold overnight. The small precipitate (if any) is collected on a 7-cm. filter containing a pad of filter-pulp pressed into the apex, washed with 1 per cent. oxalic acid solution, ignited, and weighed as thoria or rare earths or both.

The oxalic acid filtrate is treated with 20 ml. of sulphuric acid (1 : 1) and hydrogen peroxide, and the titania determined colorimetrically in an aliquot portion. The standard should contain the same quantities of sodium bisulphate, and oxalic and sulphuric acids, as the aliquot taken.[2]

(*b*) *Arsenate Method.*[3]—A quantity of finely powdered ore containing not more than 0·1 g. of zirconia is fused with potassium carbonate. The melt is extracted with hot water, the residue collected, washed, ignited, and fused with bisulphate. The filtered solution of the melt is precipitated with ammonia; the precipitate is collected, washed, and dissolved in 82 ml. of strong hydrochloric acid and 100 ml. of water. The cold solution is diluted to 360 ml., stirred, and treated with 50 ml. of 1 per cent. ammonium arsenate solution added drop by drop. The liquid is heated to boiling for 20 minutes, and 15 ml. of 10 per cent. ammonium arsenate is added from a burette. The hot solution is filtered, and the beaker cleaned with N. hydrochloric acid. The precipitate is washed and returned to the beaker with hot water. The suspension is evaporated on the water-bath until pasty, and treated with 82 ml. of strong hydrochloric acid, which is poured over the filter last used; the paper is then rinsed with 100 ml. of water, which is reserved. The precipitate is dissolved by exactly 5 minutes' boiling with the acid, after which the reserved wash-water is added. The liquid is diluted to 360 ml., left to cool, and again precipitated cold with the dilute, and hot with 10 (not 15) ml. of strong, arsenate solution. The precipitate is collected on a double filter and washed with N. hydrochloric acid followed by hot water, transferred to a tared porcelain crucible, and dried in an oven. The paper is ashed with the full flame of a Bunsen burner while the crucible is in an upright position. The last of the carbon is burned away with the crucible tilted at an angle. It is then covered with a porcelain lid, except for a small open slit, and heated in an upright position with the full flame of a Méker burner for an hour. After cooling, the ignited precipitate is weighed as $(Zr,Hf)O_2$, which is tested colorimetrically for titania.

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[1] Schoeller, *op. cit.*, p. 96, after H. Pied, *Compt. rend.*, 1924, **179**, 897.

[2] In the case of high $TiO_2$ contents, gravimetric determination of the $TiO_2$ by tannin (§ III, *e*) is more reliable.

[3] W. C. Schumb and E. J. Nolan, *Ind. Eng. Chem.*, *Anal. Ed.*, 1937, **9**, 371.

(*c*) *Selenious Acid Method.*[1]—The ore is decomposed as under (*a*) or (*b*), *above*, *i.e.* fusion with alkali carbonate followed by bisulphate fusion of the residue from the first fusion. The resultant sulphate solution is precipitated with ammonia. The washed ammonia precipitate is dissolved in 40 ml. of hydrochloric acid (1 : 1), and after addition of 20 ml. of alcohol the solution is heated, diluted to 500 ml., boiled, and precipitated with 20 ml. of 10 per cent. selenious acid (for 1 g. of ore). After standing hot for 2 hours, the precipitate is collected, lightly washed, returned with a minimum of hot water, and dissolved in 15 ml. of strong hydrochloric acid. 20 ml. of 3 per cent. hydrogen peroxide is added, the solution diluted to 500 ml., boiled, and precipitated with selenious acid; the precipitate is collected and washed as before. If thoria is known to be absent, the selenite precipitate is ignited, together with the filter-paper used in the first precipitation; the weighed zirconia is tested colorimetrically for titania.

If thoria is suspected or known to be present, the second selenite precipitate is rinsed back, as before. The two filters previously used are digested with 40 ml. of hot 10 per cent. oxalic acid; the pulp is filtered off and washed, the filtrate being added to the zirconium precipitate. The liquid (200 ml.) is boiled, treated with 12 ml. of 1 : 1 hydrochloric acid, and left in the cold for at least 10 hours, the thorium oxalate being filtered off and washed with a solution containing 20 ml. of hydrochloric acid and 25 g. of oxalic acid per litre.

If the oxalate precipitate is large, it should be decomposed by heating with strong sulphuric acid; the diluted sulphate solution is precipitated with ammonia, the precipitate collected and dissolved in hydrochloric acid, and the precipitation with oxalic acid repeated, the second filtrate being added to the first.

The filtrate or combined filtrate is evaporated with 30 ml. of sulphuric acid; the residual acid is cooled and diluted. Any precipitated selenium is filtered off; small amounts of colloidal selenium in the filtrate may be disregarded. The solution is precipitated with ammonia, the precipitate collected, lightly washed, and returned to the beaker, in which it is dissolved with 15 ml. of hot strong hydrochloric acid. Hydrogen peroxide is added as before; the solution is diluted to 500 ml., boiled, and again precipitated with selenious acid. The precipitate is collected, washed with hot water, ignited over a Méker burner, and weighed as $(Zr,Hf)O_2$. A colorimetric test for titania may be advisable.

(*d*) *Determination in Rocks.*[2]—The powdered rock (2 g.) is fused with 10 g. of sodium carbonate in platinum, and the melt disintegrated by boiling with water; the insoluble residue is collected, washed with 2 per cent. sodium carbonate solution, and boiled with a small excess of 10 per cent. sulphuric acid, the extract being filtered through the original paper. The insoluble fraction is washed with very dilute sulphuric acid, ignited in platinum, and the residue evaporated with hydrofluoric and a little sulphuric acid until strong fumes are evolved. The residual acid is diluted and filtered into the main filtrate, which should measure about 50 ml. and contain 10 per cent. of sulphuric acid by volume.

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[1] S. G. Simpson and W. C. Schumb, *Analyst*, 1931, **56**, 337.

[2] After Hillebrand and Lundell, *op. cit.*, p. 753.

Ten ml. of hydrogen peroxide and a solution of 1 g. of diammonium phosphate are added, and the solution is kept for 2 hours at about 50° C., the zirconium phosphate depositing as a flocculent precipitate. As the amount of zirconia present is usually very small, it is advisable to allow the solution to stand overnight. The precipitate is mixed with a little filter-pulp, collected on a 7-cm. paper, washed with 5 per cent. ammonium nitrate solution, ignited wet in a platinum crucible, and weighed as $ZrP_2O_7$ ($ZrO_2$ factor: 0·463).

In case of doubt, or for very accurate work, the ignited precipitate is retreated as follows: It is fused with sodium carbonate, and the melt is leached with water. The insoluble fraction is collected, washed, ignited in silica, and fused with bisulphate. The fusion is dissolved in 10 per cent. sulphuric acid and a little hydrogen peroxide, and the solution (about 20 ml.) is reprecipitated with ammonium phosphate. The precipitate is treated exactly as described *above*.

§ **VII. Complete Analysis of Zircon, Baddeleyite, and Brazilian Zirconium Ore.**—The varieties of zirconium ores encountered in metallurgical practice are at present limited to two, *viz.* Brazilian zirconia rock, and zircon sands in the form of concentrates obtained by magnetic dressing of alluvials, the zircon fraction forming the non-magnetic "reject."

The complete analysis of the Brazilian ore is by far the simpler proposition of the two, as it follows the general lines of silicate analysis, the principal difference being the resolution of the ammonia precipitate into its constituents.

The complete analysis of zircon sand, on the other hand, involves the search for and determination of such constituents as thoria, rare earths, phosphoric acid, and possibly tin and earth acids. This is due to the possible presence in the sand of subordinate quantities of monazite, cassiterite, and columbite. Ilmenite, rutile, garnet, and quartz, if present, do not call for any change in the analytical operations.

It is advisable first to test the uncrushed sand by the processes of mineralogical analysis (**II**, p. 7) to obtain a clue as to its purity and the nature of the impurities present.

(*a*) *Brazilian Zirconium Ore.*—0·25 to 0·5 g. of slimed mineral is heated in a tared platinum crucible, finally over a blast-burner, and again weighed when cold. This gives the loss on ignition.

The powder is then fused with 5 g. of sodium carbonate, or, if ferruginous, first attacked with strong hydrochloric acid and the insoluble residue from the acid extraction fused with carbonate (*cf.* § VI, *a*, *above*).

The alkaline extract is collected in a porcelain dish, treated with 1 : 1 sulphuric acid (10 ml. over and above the quantity required to neutralize the alkali), and evaporated until strong white fumes are evolved. If an extraction with hydrochloric acid was made prior to carbonate fusion, the filtered chloride solution is combined with the acidified carbonate extract before evaporation. The diluted sulphate solution is filtered, the insoluble (first silica fraction) washed and transferred to a tared platinum crucible, and the filtrate, F, reserved.

The insoluble residue from the carbonate fusion is ignited in silica and fused with potassium bisulphate, and the melt extracted with acidulated water. The solution is filtered, the filtrate being added to filtrate F, while the insoluble (second silica fraction) is added to the first, and the whole ignited and weighed. The residue is then treated with hydrofluoric and sulphuric acids as usual, the loss giving silica. The fixed small residue is fused with bisulphate, and the resultant solution added to the main filtrate, which now contains all the soluble constituents of the ore.

Double precipitation of this solution with ammonium chloride and ammonia yields the ammonia precipitate (containing zirconia, titania, ferric oxide, and alumina), and the combined filtrate therefrom is acidified, boiled down, and analysed for manganese, lime, and magnesia.

The ammonia precipitate is dissolved in hydrochloric acid, the solution saturated with hydrogen sulphide, and the small precipitate of platinum sulphide mixed with filter-pulp and removed by filtration. The filtrate is treated with tartaric acid, ammonia, and ammonium sulphide, and the ferrous sulphide collected as usual and converted into ferric oxide by known methods.

The ammoniacal tartrate filtrate is treated as described under "Titanium" (**XIII,** § III, *e*—cupferron method). The cupferron precipitate is ignited to and weighed as $(Zr,Hf)O_2 + TiO_2$; the titania in this precipitate is determined colorimetrically, and zirconia computed by difference.

The filtrate from the cupferron precipitate, containing the alumina, is boiled with nitric acid to destroy the excess of reagent, and the alumina is recovered by tannin precipitation from slightly ammoniacal solution.

(*b*) *Zircon sand* is obtained as the non-magnetic reject in the dressing of sands consisting of ilmenite, monazite, zircon, rutile, quartz, garnet, and small amounts of other silicates (*e.g.* sillimanite). The sand may contain traces of the magnetic minerals which escaped the action of the electromagnets. The process given *below* utilizes the principle of selective decomposition, 10 g. of uncrushed sand being taken.

(1) *Monazite, etc.* The sand is digested in a porcelain dish with 10 ml. of strong sulphuric acid at 200° to 250° C. for two hours, being frequently stirred with a glass rod while the attack is proceeding. The mass is left to cool, and diluted gradually with 50 ml. of cold water. The extract is filtered, and the residue washed with cold water and ignited—see (2). The filtrate is made up to bulk, and aliquot portions are used for the determination of rare earths, thoria, phosphoric acid (**XII,** § VIII), and small amounts of ferric oxide and lime.

(2) *Rutile, ilmenite, etc.* The ignited residue from (1) is weighed as a check, and fused with 20 g. of potassium bisulphate in a platinum dish until all dark particles have disappeared. The melt is extracted with 5 per cent. sulphuric acid, and the extract filtered into a 500-ml. graduated flask. The residue is washed with dilute acid and cold water, and ignited—see (3).

100 ml. of filtrate (=2 g.) is treated with 3 g. of ammonium oxalate,

warmed, nearly neutralized with ammonia, diluted with an equal volume of saturated ammonium chloride solution, and precipitated with tannin (**XIII**, § III, *d*). The red tannin precipitate is ignited and weighed as $TiO_2$; the filtrate, after having been tested for complete precipitation of the titania, is made up to 500 ml., and 125 ml. (= 0·5 g.) transferred to a 400-ml. beaker. This solution (which contains iron and a little zirconia) is boiled and precipitated with more tannin and a slight excess of ammonia. The precipitate, P, is collected, washed, ignited, and reserved (see *below*).

(3) *Zircon, quartz, etc.* The ignited residue from (2) is weighed and finely crushed, and one-twentieth of its weight (equivalent to 0·5 g. of original sand), together with the precipitate P obtained under (2), is fused in a platinum crucible with 5 g. of sodium carbonate, the analysis being conducted throughout as described under (*a*), *above.*

## XV.—THORIUM.

§ **I. Minerals.**—All thorium minerals are radioactive.

(*a*) *Oxides.*—(1) *Thorianite* is essentially thorium oxide, $ThO_2$, containing uranium oxide (10 to 30 per cent.) and rare earths (1 to 8 per cent.). Jet-black, lustrous, rhombohedral crystals of cubic habit. Brittle. H. 7; sp. gr. 8 to 9·7. Evolves helium on heating.

(2) *Mackintoshite* is a complex mixture containing about 45 per cent. of thoria, together with oxides of uranium, zirconium, tantalum, iron, magnesium, lead, and sodium. Black, opaque, tetragonal crystals resembling thorite (*q.v.*). H. 5½; sp. gr. 5·4.

(3) *Cleveite*, *bröggerite*, and *uraninite* are uranium minerals containing variable amounts of thoria (see **XXII**, § I).

(*b*) *Silicates.*—(1) *Thorite* and *orangite* are varieties of thorium silicate, $ThSiO_4$, differing in colour and specific gravity. Orangite is heavier (5·2 to 5·4) than thorite (4·4 to 4·8); the former possesses a fine orange colour, while the latter is dark brown to black. Both crystallize in the tetragonal system, and are isomorphous with zircon, rutile, and cassiterite. H. 4½ to 5. Uranium oxide and rare earths often present.

(2) *Calciothorite* is a deep red, translucent, amorphous variety of thorite containing lime. H. 4½; sp. gr. 4·1.

(3) *Eucrasite* is a black, opaque mineral resulting from the alteration of thorite. H. 4½ to 5; sp. gr. 4·4. It is usually found amorphous, and contains large amounts of rare earths.

(4) *Freyalite* is a brown, amorphous, resinous silicate containing thoria: 28 per cent., cerium earths: 30 per cent., and zirconia: 6 per cent. H. 6; sp. gr. 4·1.

(5) *Pilbarite*, *thorogummite*, and *yttrogummite* are yellow to brown, opaque silicates of thorium and uranium (see **XXII**, § I).

(*c*) *Phosphates.*—(1) *Monazite.* A phosphate of the cerium metals and thorium. Small, yellow, brittle, monoclinic crystals, with a resinous lustre, usually translucent. H. 5; sp. gr. 5 to 5·2. Occurs generally as water-worn, yellow, translucent grains in alluvial deposits, together with quartz, ilmenite, rutile, and garnet. It is the most important source of thorium. Magnetic, but less so than ilmenite.

(2) *Xenotime.* A phosphate of yttrium metals with a small amount of thorium. See **XII,** § I, *b*, 3.

§ **II. Properties and Compounds.**—(*a*) The *metal* is a dark grey powder of sp. gr. 11·5 and melting-point 1850° C. It readily combines with oxygen, hydrogen, and nitrogen, and dissolves in *aqua regia*, but with difficulty in other acids.

(*b*) The *oxide*, $ThO_2$, prepared by ignition of the hydroxide, oxalate or nitrate, is a dense white powder, remaining white when heated, insoluble in acids, except boiling strong sulphuric acid, and soluble in fused bisulphate. It crystallizes in the tetragonal system when fused with borax, and in the octahedral system when fused with sodium phosphate. The oxide formed by igniting the nitrate containing 1 per cent. of sulphate is a voluminous white powder, which is used in the mantle industry.

(*c*) *Thorium hydroxide*, $Th(OH)_4$, is formed as a white, amorphous precipitate on addition of ammonia or alkali hydroxides to solutions of thorium salts; it is insoluble in excess of the reagents. Barium carbonate in cold, or sodium thiosulphate in boiling, solutions causes complete precipitation of the hydroxide. The thiosulphate reaction distinguishes thorium from the rare earths.

(*d*) *Thorium peroxide* is precipitated in the form of a gelatinous colourless peroxynitrate by 6 per cent. hydrogen peroxide, added to a neutral solution of thorium nitrate; it is decomposed by acids, and yields the dioxide on ignition.

(*e*) *Thorium fluoride*, $ThF_4.4H_2O$, is a white, gelatinous precipitate, insoluble in water or mineral acids, formed by hydrofluoric acid in a solution of the chloride.

(*f*) *Thorium chloride*, $ThCl_4.8H_2O$, is soluble in water, alcohol, and ether.

(*g*) *Thorium iodate*, $Th(IO_3)_4$, is a white, amorphous precipitate, insoluble in nitric acid in presence of a large excess of alkali iodate.

(*h*) *Thorium sulphate*, $Th(SO_4)_2$, is very important commercially, since it is the salt used to prepare pure thorium compounds. It forms supersaturated solutions at 0° C., which, on heating, deposit the octahydrate at 20° C., and the tetrahydrate above 43° C.

(*i*) *Thorium nitrate*, $Th(NO_3)_4.12H_2O$, is very soluble in water and alcohol. Important in the incandescent-mantle industry.

(*j*) *Thorium oxalate*, $Th(C_2O_4)_2.6H_2O$, forms as a white crystalline precipitate when acid solutions of thorium salts are treated with oxalic acid; it is insoluble in water, oxalic acid, or dilute acids, but soluble in alkali oxalate solutions, from which it is reprecipitated by addition of mineral acids. On ignition it affords the dioxide.

(*k*) *Thorium carbonate* is a white amorphous precipitate produced by alkali carbonates. It is soluble in excess of precipitant; the solution becomes turbid when heated, but clears again on cooling.

§ **III. Quantitative Separation.**—Precipitation with oxalic acid from a slightly acid solution separates thorium from all the other members of the ammonia group (including titanium and zirconium), except the rare earths. Several methods are available for the separation of thorium from the rare earths; the following are the most rapid and convenient:

(*a*) *Hydrogen Peroxide Method.*[1]—The nitrate solution free from sulphates and chlorides is evaporated to dryness on the water-bath, the residue is moistened with water and dried again, and the resulting nearly neutral nitrates are dissolved in 100 ml. of 10 per cent. ammonium nitrate solution. The solution is heated to 60° to 70° C. and treated with 3 per cent. hydrogen peroxide (free from phosphates and sulphates) until no further gelatinous precipitate of thorium peroxide is formed. The precipitate is collected on a No. 41 Whatman paper, washed with 2 per cent. ammonium nitrate solution, and rinsed back into the beaker; a few ml. of nitric acid are added, and the solution is boiled to decompose the peroxide and evaporated to dryness to expel the excess of nitric acid. The thorium is then reprecipitated as before; the rare earths are recovered from the filtrate by addition of an excess of ammonia.

(*b*) *Iodate Method.*[2]—The solution (100 ml.), which may contain sulphuric and phosphoric acids, is treated with 50 ml. of concentrated nitric acid while cooling, and then with 100 ml. of a 15 per cent. solution of potassium iodate in 1 : 1 nitric acid. The mixture is stirred occasionally for half an hour, then set aside to allow the precipitate to settle; the clear liquor is decanted through a filter, and the precipitate rinsed on with a 1 per cent. solution of potassium iodate in 10 per cent. nitric acid. After one wash with this solution the precipitate is returned to the beaker, beaten up with 50 ml. of the same solution, and again rinsed on to the filter, where it is washed three times with the same solution. The precipitate is then redissolved in 30 ml. of hot concentrated nitric acid, and reprecipitated by addition of 4 g. of iodate dissolved in 1 : 1 nitric acid to the cooled solution diluted with an equal volume of water. The precipitate is collected and washed as before, and then dissolved in hydrochloric acid with the aid of a little sulphur dioxide solution. This solution contains all the thorium and any zirconium and titanium originally present; it is boiled with a slight excess of ammonia, the washed hydroxides are dissolved in 10 ml. of hydrochloric acid, and the thorium is precipitated free from other metals by the oxalate method described in § IV.

(*c*) *Thiosulphate Method.*[3]—The chloride solution, containing not more than 0·2 to 0·3 g. of thoria, is evaporated to dryness on the water-bath, the residue moistened with water, dried again, and then dissolved in 200 ml. of hot water, and the resulting solution treated cold with 5 g. of sodium thiosulphate and heated slowly to 80° to 90° C. with occasional stirring. The beaker is placed on the water-bath, and the precipitate is allowed to settle for 30 minutes, then filtered on a No. 41 Whatman paper, washed with warm water, and returned to the beaker with the minimum of hot water; 5 ml. of hydrochloric acid is added, the mixture boiled to dissolve the thoria, and the solution filtered through the same paper to remove the sulphur. The filtrate is collected in a 200-ml. glass dish and evaporated to dryness on the water-bath. The thoria is then reprecipitated as before, except that only 3 g. of thiosulphate is required; after a further repetition of the whole process the thoria precipitate is free from rare earths. This third precipitate is extracted with 5 ml. of hydrochloric acid, and the thorium in the filtered solution is precipitated as oxalate as described in § IV. The three filtrates from the thiosulphate precipitates are united and boiled for one hour, any small precipitate thus produced being collected and ignited together with the three sulphur residues. The resulting oxides are dissolved by fusion with a small piece of potassium bisulphate in a silver crucible, the melt is dissolved in hot water, the unfiltered solution boiled with a slight excess of sodium hydroxide, and the washed precipitate dissolved in hydrochloric acid; this solution is evaporated, and any small amount of thoria contained therein recovered by boiling with thiosulphate. The precipitate is usually very small, so that it is sufficient to extract it with a few ml. of hydrochloric acid and to precipitate the thoria in the filtered extract by addition of oxalic acid, keeping the volume as low as possible.

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[1] E. Benz, *Zeitsch. angew. Chem.*, 1902, **15**, 297.
[2] R. J. Meyer and M. Speter, *Chem. Zeit.*, 1910, **34**, 306.
[3] E. White, *Thorium and Its Compounds*, Institute of Chemistry, 1912.

(*d*) *Hexamethylenetetramine* (*Hexamine*) *Method.*[1]—This method depends on the fact that thoria is a very weak base and is completely precipitated at a *p*H of about 6·5, whereas the rare earths are strong bases.

The chloride solution is cautiously treated with 1 : 10 ammonia until a faint permanent turbidity is produced, which is then cleared by the addition of a few drops of 1 : 1 hydrochloric acid; the solution is diluted to 200 ml., treated with 10 g. of ammonium chloride, heated to 70° to 80° C., and the thoria precipitated by the slow addition of a 2 per cent. solution of hexamine until no further turbidity is produced. The precipitate is collected on a loose filter-paper, washed with warm 5 per cent. ammonium chloride solution, returned to the beaker, and dissolved by the addition of a few drops of hydrochloric acid. The solution is neutralized, diluted, and treated with ammonium chloride and hexamine as before; a third precipitation is advisable if the amount of rare earths present is considerable. The final hexamine precipitate is dissolved in hydrochloric acid, and the thoria precipitated as oxalate as described in § IV. Zirconia and titania accompany the thoria in the hexamine process, but are eliminated by the oxalate precipitation.

§ **IV. Gravimetric Determination.**—Thorium is always determined gravimetrically as the dioxide obtained by ignition of the oxalate. The precipitation as oxalate is best carried out as follows:

The solution of thorium chloride obtained as described in § III, *b*, *c*, or *d* is nearly neutralized with ammonia, a permanent precipitate being avoided, diluted to 100 ml., heated to boiling, and treated with a hot solution of 4 g. of ammonium oxalate. The resulting clear solution is treated drop by drop with 1 : 1 hydrochloric acid with stirring until a permanent turbidity is produced; a further 10 ml. of the same acid is then added slowly and the mixture set aside overnight to cool. This procedure gives a readily filtrable crystalline precipitate of thorium oxalate, whereas direct precipitation with oxalic acid frequently yields a microcrystalline precipitate which filters very slowly and often runs through the paper. The precipitate is washed with warm 2 per cent. oxalic acid solution and ignited wet to thoria, which should be perfectly white, both hot and cold.

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[1] A. M. Ismail and H. F. Harwood, *Analyst*, 1937, **62**, 185.

§ **V. Detection in Ores.**—The mineral is decomposed by heating with concentrated sulphuric or hydrochloric acid, or by fusion with potassium bisulphate. If sulphuric acid is used, the reaction product is extracted with cold water to give a 10 per cent. acid solution, from which the rare earths and thoria are precipitated by addition of oxalic acid. If hydrochloric acid is used, the solution is evaporated to dryness, the residue heated to dehydrate silica and extracted with 5 per cent. hydrochloric acid, the filtered solution precipitated with ammonia, the washed precipitate redissolved in hydrochloric acid, and the solution treated with oxalic acid. If bisulphate fusion is used the melt is extracted with hot 5 per cent. ammonium oxalate solution, and the filtered extract treated with hydrochloric acid in excess to precipitate thorium (and scandium) oxalate.

The oxalate precipitate obtained by any of the above procedures is boiled with an excess of potassium hydroxide to convert the metals into hydroxides, which are collected, washed, and dissolved in dilute nitric acid. The resulting solution is tested for thorium as follows:

(1) Neutralization with ammonia, avoiding a permanent precipitate, and addition of 6 per cent. hydrogen peroxide produces a gelatinous colourless precipitate of peroxynitrate.

(2) Addition of a 10 per cent. solution of potassium iodate in 1 : 1 nitric acid yields a white flocculent precipitate.

(3) Addition of sodium acetate and tannin gives a white gelatinous precipitate.

(4) Addition of ammonium oxalate affords a white crystalline precipitate, soluble in excess, and reprecipitated by addition of acid. This test is not very sensitive in the presence of much rare earths.

(5) Boiling with sodium thiosulphate produces a white flocculent precipitate; extraction of this precipitate with hydrochloric acid yields a solution of thorium chloride, which gives a gelatinous precipitate with ammonium fluoride.

Tests 1 and 2 distinguish thorium from the rare earths and scandium; test 4 distinguishes thorium from zirconium and titanium; and tests 1, 2, and 3, thorium from the rare earths.

§ **VI. Determination in Ores.**—(*a*) *Monazite.*—5 g. of uncrushed sand is heated in a porcelain basin with 20 ml. of sulphuric acid with occasional stirring to avoid caking; the temperature should be just high enough to produce a slight evolution of acid fumes. After 2 to 3 hours all yellow grains should have disappeared; this may be ascertained by mixing a little of the reaction product with cold water on a watch-glass and examining the sandy residue with a pocket lens. The thick mass is then allowed to cool and stirred into 200 ml. of cold water, and the solution is decanted from insoluble sand (white grains of zircon or quartz and black grains of rutile or ilmenite) into a 500-ml. graduated flask and diluted to the mark. The solution is filtered through a dry paper, and 200 ml. (= 2 g.) is pipetted into a beaker; the thorium and rare earths are then precipitated by addition of 180 ml. of a cold saturated solution of oxalic acid. Next morning the precipitate is collected, washed with cold 2 per cent. oxalic acid, and ignited. The residual oxides are dissolved in hydrochloric acid, and the precipitation with oxalic acid is repeated (see **XII,** § III, *a*). The second oxide residue is dissolved in hydrochloric acid, and the thorium separated by the thiosulphate or hexamine method (§ III, *c* or *d*); or in nitric acid and hydrogen peroxide for the separation of thorium by the peroxide method (§ III, *a*).

If the iodate method is to be used the solution of the sand should be made up to 250 ml., and 100 ml. (= 2 g.) taken for the determination, which is carried out as described in § III, *b*.

(*b*) *In Thorite and Silicates rich in Thoria, but poor in Rare Earths.*—The finely ground mineral (1 g.) is digested with 10 to 15 ml. of concentrated hydrochloric acid on the water-bath, the solution is taken to dryness, the residue heated at 110° C. to dehydrate the silica, and the soluble material extracted with 2 ml. of concentrated hydrochloric acid and 30 to 40 ml. of hot water. The silica is filtered off and treated with hydrofluoric acid, and any residue is fused with potassium bisulphate; the melt is extracted with a hot solution of 3 g. of ammonium oxalate, and after filtration the solution is reserved. The main chloride solution is saturated with hydrogen sulphide, any precipitate of copper or lead sulphide filtered off, and the filtrate boiled to expel hydrogen sulphide and then oxidized with a few drops of nitric acid. While still boiling, the reserved oxalate solution from the treatment of the silica is added, followed by 10 ml. of 1 : 1 hydrochloric acid to precipitate all the thorium as oxalate. Next morning the precipitate is collected, well washed with hot water, and ignited. The oxide residue is fused with 5 g. of potassium bisulphate in a silica crucible, the melt disintegrated by boiling with water containing a few drops of sulphuric acid, and the solution (which contains thorium potassium sulphate in suspension) poured into 50 ml. of boiling 10 per cent. sodium hydroxide solution. After boiling the mixture with stirring for 5 to 10 minutes, 200 ml. of hot water is added, the precipitate allowed to settle, and the clear liquid decanted through a Whatman No. 41 filter, and finally the precipitate is thoroughly washed with boiling water and redissolved in hydrochloric acid for the separation of thoria by the thiosulphate method. Generally the amount of thoria present is too large for convenient handling by any of the other methods of separation.

(*c*) *In Thorianite and Similar Oxide Minerals.*—The finely ground mineral (1 g.) is fused with 8 g. of potassium bisulphate in a silica crucible, the melt extracted with a hot solution of 5 g. of ammonium oxalate, and the insoluble material filtered off and washed with hot 1 per cent. ammonium oxalate solution. Most of the thorium is in the filtrate as the double ammonium oxalate, but a small amount may be occluded by the rare-earth oxalates, which are chiefly in the insoluble portion; to recover this the insoluble material is ignited, the rare earths are extracted by digestion with hydrochloric acid, and the thorium is separated from the solution by neutralizing with sodium carbonate and boiling with thiosulphate. The washed thiosulphate precipitate is extracted with hot dilute hydrochloric acid, the filtered extract is neutralized with ammonia, a permanent precipitate being avoided, and the solution is added to the original ammonium oxalate solution containing the bulk of the thoria. The combined solution is treated with 10 ml. of hydrochloric acid to recover the thorium oxalate, and the precipitate is treated as described under (*b*), *above*.

§ **VII. Complete Analysis of Ores.**—(*a*) *Monazite*.—See **XII,** § VIII.

(*b*) *Thorite and its Alteration Products and Varieties*.—The ore is decomposed as described in § VI, *b*, and copper and lead are determined in the hydrogen-sulphide precipitate.

The siliceous residue may contain barium sulphate, as well as tantalic and niobic oxides and a little thoria; silica is determined by evaporation with hydrofluoric and sulphuric acids. The residue is fused with bisulphate, the melt extracted with hot 5 per cent. ammonium oxalate, and the barium sulphate filtered off. The oxalate filtrate is just neutralized with ammonia (methyl red), and the tantalum and niobium precipitated with tannin. The filtrate is treated with a slight excess of ammonia and more tannin, and the precipitate, which contains all the other metals likely to be present, is ignited; the resulting oxides are heated with a few drops of concentrated sulphuric acid, then more strongly at 400° to 500° C. The sulphates are dissolved in cold water, the solution is combined with the oxidized solution from the hydrogen-sulphide treatment, and boiled with 5 g. of ammonium chloride and an excess of ammonia free from carbonate. The filtrate is used for the determination of lime and magnesia, and the precipitate for the determination of thoria, rare earths, iron, alumina, uranium, etc. Thoria and the rare earths are precipitated from the hydrochloric-acid solution of the hydroxides by means of oxalic acid, titanium by neutralization of the oxalate filtrate and addition of tannin (**XIII,** § III, *d*), and the other metals by ammonium acetate and more tannin added to the titanium filtrate. For the separation of zirconium and uranium from iron and aluminium, see **XXII,** § III.

(*c*) *Thorianite*.—The mineral is fused with bisulphate, the melt extracted with ammonium oxalate solution, and the tantalum, niobium, and titanium recovered with tannin (**XIII,** § III, *d*). Thorium is precipitated by acidifying the tannin filtrate (§ IV), and the other bases by addition of ammonium acetate and tannin (**XIII,** § IV, *c*). Silica, barium sulphate, and heavy metals are determined as under (*b*), *above*.

## XVI.—GERMANIUM.

§ **I. Minerals.**—(*a*) *Argyrodite*, silver germanium sulphide, $4Ag_2S.GeS_2$, is a steel-grey metallic-looking mineral occurring in small indistinct monoclinic crystals or compact masses. It gives a shining grey-black streak. H. 2·5; sp. gr. 6.

(*b*) *Canfieldite* is a variety of the above, in which part of the germanium is replaced by tin. It is of a somewhat darker colour, and has a brilliant metallic lustre. H. 2·5; sp. gr. 6·3.

(*c*) *Germanite*, substantially $10Cu_2S.4GeS_2.As_2S_3$, has been found in a S.W. African locality.[1] It is a dark grey, lustrous mineral with a reddish tinge, and contains more gallium than any other mineral. Sp. gr. 4·46.

(*d*) *Ultrabasite*, mercury germanium lead thioantimonite; grey-black, orthorhombic. H. 5; sp. gr. 6·03.

[1] F. W. Kriesel, *Chem. Zeit.*, 1924, **48**, 961.

(*e*) Germanium is often found in minute quantities in zinc blende.

§ **II. Properties and Compounds.**—(*a*) The *metal* is greyish-white, brittle, and lustrous. It melts at 958° C., and has a sp. gr. of 5·47. It is soluble in *aqua regia*, but not in hydrochloric acid. Nitric acid converts it into the dioxide. It may be prepared by reduction of the oxide with hydrogen or magnesium, or by the action of hydrogen or sodium on potassium fluorogermanate.

(*b*) *Germanous hydroxide*, $Ge(OH)_2$, is formed on addition of alkali to an acid solution of the corresponding chloride as a yellow precipitate, slightly soluble in water to a yellow solution. With excess of alkali it gives soluble germanite. On being heated in the liquor from which it is precipitated it turns red, and this compound is believed to be the germanium analogue of formic acid, $HGeOOH$, as the same compound is formed on the addition of water to germanium chloroform, $HGeCl_3$.

(*c*) *Germanium dioxide*, $GeO_2$, is a dense, white, difficultly fusible powder. It dissolves in 250 parts of water at ordinary temperature, and in 95 parts at 100° C.; soluble both in acids and alkalis. It is formed on treating the metal or the sulphide with nitric acid.

(*d*) *Germanous sulphide*, $GeS$, is produced by a current of hydrogen sulphide in a solution of the dichloride as a red-brown precipitate soluble in alkalis and in concentrated hydrochloric acid. It is also slightly soluble in water.

(*e*) *Germanic sulphide*, $GeS_2$, is thrown down as a white precipitate when a strongly acid solution of the dioxide in hydrochloric acid is saturated with hydrogen sulphide. It is soluble in 222 parts of cold water, but almost insoluble in concentrated hydrochloric acid. With alkalis it gives thiogermanates, which are not decomposed by weak acids like acetic, but require a considerable excess of mineral acid for complete decomposition.

(*f*) *Germanium chlorides.*—Both the di- and tetra- chlorides are volatile liquids readily decomposed by water, with the separation of the corresponding hydrated oxides. The tetrachloride boils at 86° C.

(*g*) *Potassium fluorogermanate*, $K_2GeF_6$, separates from a solution of the dioxide in hydrofluoric acid on the addition of potassium fluoride as a jelly (*cf.* $K_2SiF_6$), which slowly crystallizes. One part is soluble in 174 parts of cold and 34 parts of boiling water.

§ **III. Quantitative Separation.**—The separation of germanium from other metals depends on the following reactions:

(1) The volatility of germanium tetrachloride, which can be distilled even from hydrochloric acid solutions in the presence of chlorine and powerful oxidizing agents.

(2) The insolubility of the tannin complex in dilute mineral acids (molybdenum, tungsten, tantalum, and niobium interfere).

(3) The solubility of the disulphide in alkaline sulphide solutions and its insolubility in 6N. mineral acids.

(*a*) *Separation by Distillation.*[1]—The solution, which should be free from halogen acids, is evaporated to a low volume, cooled, and transferred to a distilling flask fitted with a rubber stopper carrying a tube for introducing chlorine and a rectifying column connected to a condenser and a receiver cooled in ice-water. An equal volume of concentrated hydrochloric acid is added to the solution, and a slow current of chlorine passed through the apparatus; heat is now applied until the solution boils gently, and distillation is continued until half the liquid has distilled over. An equal volume of hydrochloric acid is added to the cooled solution in the distilling flask, and the operation repeated as before; it may be necessary to distil a third time, but this distillate should be tested separately for the presence of germanium by the tannin method described *below.*

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[1] L. M. Dennis and E. D. Johnson, *J. Amer. Chem. Soc.*, 1929, **51**, 1459.

(*b*) *Precipitation with Tannin.*[1]—(1) The solution is treated with sulphuric acid until it is 0·5 to 1·0N. in free acid, then with 8 to 10 g. of ammonium sulphate, and, after heating to boiling, with 10 to 20 ml. of 10 per cent. tannin solution added slowly with stirring; finally, a further 2 to 3 g. of ammonium sulphate is added, the solution is allowed to cool, and the flocculent white precipitate collected on a No. 40 Whatman paper with the aid of gentle suction and washed thrice with hot 5 per cent. ammonium nitrate solution containing 5 ml. of 2N. nitric acid per 100 ml. The precipitate is rinsed back into the beaker with the wash-liquor, thoroughly beaten up, and refiltered; it is now washed thoroughly with the same solution, sucked as dry as possible on the pump, and transferred to a tared crucible. Ignition is carried out at as low a temperature as possible, preferably on an asbestos gauze; when all is thoroughly charred the crucible is transferred to a muffle maintained at about 600° to 650° C., and heated until all the carbon is removed. After cooling, the residue is moistened with a few drops of nitric acid, dried on the water-bath, and again heated to about 600° C. until perfectly white; the temperature is then raised to 1000° C. for a short time and, after cooling, the $GeO_2$ is weighed. Too rapid heating must be avoided throughout, since $GeO_2$ in contact with carbonaceous matter is reduced to GeO, which is volatile above 700° C. This method separates germanium from arsenic, copper, cadmium, zinc, the ammonia and ammonium-sulphide group metals, and the alkaline earths in one precipitation.

(2) It is usually recommended to precipitate the germanium from the acid chloride distillate by saturating it with hydrogen sulphide, but this is a tedious operation and the precipitate filters badly. We recommend diluting the distillate with an equal volume of water and adding ammonia slowly while cooling under ice-water until the solution is just ammoniacal; the solution is then acidified with acetic acid, and the germanium precipitated with tannin.

(*c*) *Precipitation with Hydrogen Sulphide.*—Germanium disulphide is completely precipitated by hydrogen sulphide only from solutions which are 5N. in sulphuric acid or 3·5N. in hydrochloric acid.[1] When other metals of the hydrogen-sulphide group are present, it is probable, however, that precipitation of the germanium is complete over a wider range of acidity. In the absence of such metals flocculation of the germanium sulphide may take many hours, in fact some authors recommend saturating the solution with the gas and setting it aside in a stoppered flask for 48 hours. The precipitate should be washed with 5N. sulphuric acid saturated with hydrogen sulphide.

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[1] G. R. Davies and Sir Gilbert Morgan, *Analyst,* 1938, **63,** 388.

Digestion of a mixed sulphide precipitate with sodium sulphide removes the germanium with the arsenic, antimony, and tin, leaving the copper, bismuth, lead, and cadmium sulphides insoluble. Exact neutralization of the solution with acetic acid reprecipitates the arsenic, antimony, and tin, but not the germanium; retreatment of this precipitate with alkali sulphide and acetic acid is advisable for complete separation. The germanium filtrate is boiled with ammoniacal hydrogen peroxide to oxidize sulphides, and treated with 2 to 3 ml. of acetic acid and tannin to precipitate the germanium.

Arsenic and antimony may also be separated from germanium by adding a few ml. of hydrofluoric acid to the solution to convert the germanium into fluorogermanate, and then saturating with hydrogen sulphide to precipitate the arsenic and antimony, fluorogermanate like fluorostannate being unaffected by hydrogen sulphide. A better method, which can be carried out in glass apparatus, consists in precipitating the arsenic and antimony with hydrogen sulphide in the presence of 10 g. of oxalic acid, which prevents precipitation of tin and germanium. Both metals can be recovered from the filtrate by boiling off the hydrogen sulphide, just neutralizing with ammonia, adding 2 to 3 drops of acetic acid, and precipitating with tannin (*b*, *above*).

§ **IV. Gravimetric Determination.**—(*a*) *As Magnesium Germanate.*—This method, originally proposed by J. H. Müller,[1] has been recently investigated and improved by Davies and Morgan,[2] who recommend the following procedure:

The dilute sulphuric acid solution (100 ml.) is treated with 24 to 30 ml. of 2N. ammonium sulphate solution, an excess of 2 to 3 ml. of N. magnesium sulphate solution over that required to form $Mg_2GeO_4$ (see *below*), and 15 to 20 ml. of concentrated ammonia, boiled for one minute, and set aside for 3 to 4 hours. The precipitate is collected in a porous porcelain crucible, washed with 25 to 30 ml. of 1 : 9 ammonia, ignited, and weighed as $Mg_2GeO_4$, which contains 39·2 per cent. of germanium. For good results it is essential to have a rough idea of the amount of germanium in the solution; if this is unknown the precipitate should be redissolved in 7 to 10 ml. of warm 2N. sulphuric acid, the solution nearly neutralized with ammonia and diluted to 100 ml., and the germanium reprecipitated by adding 15 ml. of 2N. ammonium sulphate, 1 ml. of N. magnesium sulphate, and 15 to 20 ml. of ammonia, and boiling. The precipitate is collected, washed, and ignited as before.

(*b*) *With Tannin.*—This has been described in § III, *b*; it is probably the best method for general gravimetric work. Precipitation can be made in nitric or sulphuric acid solutions, acid acetate solutions, and nearly neutral oxalate solutions; with due precautions the precipitate can be ignited directly to oxide for weighing, the small amount of reduction which occurs being overcome by treating the ignited precipitate with nitric acid and re-igniting. Alternatively, the precipitate and paper may be moistened with a few drops of sulphuric acid and successive small portions of nitric acid while being cautiously heated; when most of the carbon has been removed the residual acid is slowly evaporated off, and the residue heated gently at first, finally at 1000° C., and weighed as $GeO_2$.

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[1] *J. Amer. Chem. Soc.*, 1922, **44**, 2496.

[2] *Loc. cit.*

(*c*) *As Cinchonine Germanomolybdate.*[1]—This method is suitable for the determination of not more than 5 mg. of germanium, and is especially useful in the analysis of coal and plant-ash and similar material containing only traces of the element, since the compound weighed contains only a little over 2 per cent. of germanium.

The neutral solution (40 ml.) is treated with 20 ml. of 25 per cent. ammonium nitrate solution, 16 to 18 ml. of 2 per cent. ammonium molybdate solution, 20 ml. of 2N. nitric acid, and, with stirring, 9 to 10 ml. of a 2·5 per cent. solution of cinchonine in 0·25N. nitric acid, and set aside with occasional stirring for 2 to 4 hours or until opalescence ceases to increase for 30 minutes after stirring. The precipitate is collected on a glass filter-crucible, washed with 2·5 per cent. ammonium nitrate solution containing 5 ml. of 2N. nitric acid per 100 ml., dried at 160° C. for 2 hours, and weighed as $(C_{19}H_{22}ON_2)_4H_4.GeMo_{12}O_{40}$, which contains 2·385 per cent. Ge.

§ **V. Detection in Ores.**—(*a*) *Sulphide ores* are decomposed by heating with nitric and sulphuric acids; the insoluble material is filtered off and digested with ammonium sulphide, and the filtered extract boiled with hydrogen peroxide and added to the original acid solution, which is then neutralized with ammonia, treated with 10 ml. of concentrated sulphuric acid and 15 g. of ammonium sulphate, diluted to 500 ml., and precipitated at the boiling-point with a 10 per cent. solution of tannin. The tannin precipitate is collected and ignited as described in § III, *b*, the residue is digested with a little 5 per cent. sodium hydroxide solution, and the solution is saturated with hydrogen sulphide and filtered. The filtrate is made just neutral with dilute sulphuric acid and set aside overnight in a stoppered flask; next morning any precipitate is filtered off, the acidity adjusted to 5N. to 6N. by addition of sulphuric acid, and the solution saturated with hydrogen sulphide. A white flocculent precipitate indicates the presence of germanium.

(*b*) *Roasted zinc ores* are dissolved by heating with an excess of hydrochloric acid in a small distillation flask connected with a well cooled condenser and receiver. Heating is continued until all soluble material has dissolved, and the solution is then vigorously boiled until about half its volume has distilled over. The distillate is diluted with an equal volume of water, 20 g. of ammonium acetate added, followed by ammonia until the solution is alkaline, then by 2 to 3 ml. of acetic acid, and a 10 per cent. solution of tannin is poured in slowly with stirring; a white flocculent precipitate indicates the presence of germanium.

Traces of germanium occur in many zinc ores, and in the hydrometallurgical extraction of zinc from these ores the germanium must be eliminated before the zinc sulphate solution is passed to the electrolytic cells, since it has a serious effect on the rate of deposition of the zinc and on the nature of the deposit.

§ **VI. Determination in Ores.**—(*a*) *Germanite and Other Sulphide Ores.*—One g. of the finely powdered mineral is dissolved by heating with

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[1] Davies and Morgan, *loc. cit.*

10 to 15 ml. of 1 : 1 nitric acid and 1 to 2 ml. of sulphuric acid; when red fumes cease to be evolved the liquid is evaporated to a low volume (about 5 ml.), diluted to 50 ml. with hot water, and filtered. The residue is well washed with hot water, rinsed back into the beaker, and digested with a little ammonium sulphide solution to extract any germanium dioxide that did not dissolve in the acid; this solution is filtered through the same paper, and the insoluble, which may contain lead sulphide, is washed with very dilute ammonium sulphide solution. The sulphide filtrate is boiled, oxidized with hydrogen peroxide, again boiled to decompose excess of peroxide, and added to the original filtrate. The whole is diluted to 400 ml., treated with 15 ml. of 1 : 1 sulphuric acid and 10 g. of ammonium sulphate, and heated to boiling; the germanium is then precipitated by the addition of 20 to 30 ml. of 10 per cent. tannin solution followed by a little more ammonium sulphate. After cooling, the precipitate is collected under gentle suction on a large filter-paper, well washed with 2 per cent. ammonium nitrate solution, and ignited to $GeO_2$ as described in § III, *b*, 1. To test for purity, the weighed precipitate may be dissolved in 2 per cent. sodium hydroxide solution; if there is any residue it should be filtered off, and the germanium in the filtrate reprecipitated with tannin as described *above*.

If the ore contains silver (canfieldite), the nitrate-sulphate filtrate obtained in the first step is heated to boiling and treated drop by drop with a 2 per cent. solution of potassium thiocyanate until no further white precipitate forms. The filtrate from the silver thiocyanate is then combined with the oxidized sulphide extract of the insoluble, and the germanium separated as described *above*.

If it is desired to determine the other constituents in the ore, it is better to remove the germanium first by distillation. In this case the solution obtained from the nitric-sulphuric acid attack is evaporated without filtering until all the nitric acid is expelled, diluted, and transferred to a small distillation flask with the minimum amount of water; an equal volume of hydrochloric acid is added and the liquid distilled as described in § III, *a*, the germanium being recovered from the distillate by the tannin method (§ III, *b*, 2).

(*b*) *Blende.*—The mineral (50 to 100 g.) is weighed into a large beaker, covered with water, and treated slowly with nitric acid until completely decomposed; the resulting solution is evaporated to dryness in a porcelain dish, and the dish is then placed in a cold muffle, the temperature of which is gradually raised until the nitrates are completely decomposed. The residual oxide cake is powdered roughly, placed in a large distilling flask, and treated with 200 ml. of strong hydrochloric acid; the mixture is heated to boiling, and the germanium distilled over as described in § V, *b*. It is advisable to add a little potassium permanganate to the flask during distillation to assist in preventing any arsenic from passing over with the germanium. If the latter is finally precipitated with tannin, the small quantity of arsenic which may have distilled does not interfere.

# XVII.—VANADIUM.

§ **I. Minerals.**—(*a*) *Sulphides.*—(1) *Patronite*, vanadium sulphide approximating to the composition $VS_4$ or $V_2S_9$, is an amorphous black mineral of sp. gr. 2·5; H. 5. This complex carbonaceous ore occurs in association with vanadiferous asphalt. The ash of many coals and asphalts contains vanadium.

(2) *Bravoite*, vanadiferous iron nickel sulphide; pale yellow octahedra with a faint pink tarnish.

(3) *Sulvanite*, cuprous orthothiovanadate, $3Cu_2S.V_2S_5$, usually occurs as compact bronze-yellow metallic-looking masses giving a black streak. H. 3·5; sp. gr. 4.

(*b*) *Silicates.*—(1) *Ardennite*, a manganese epidote containing vanadium sesquioxide. Yellow-brown orthorhombic prisms terminated by pyramids; faces strongly striated. H. 6·5; sp. gr. 3·6.

(2) *Roscoelite*, vanadium mica, $2H_2O.(K,Na)_2O.(Al,V)_2O_3.6SiO_2$, resembles muscovite in physical properties, but its colour is clove-brown or olive-green.

(*c*) *Anhydrous Vanadates.*—(1) *Pucherite*, bismuth orthovanadate, $BiVO_4$, a translucent red-brown mineral with vitreous to adamantine lustre and yellow streak. Small orthorhombic tables. H. 4; sp. gr. 6·2.

(2) *Vanadinite*, $3Pb_3(VO_4)_2.PbCl_2$, lead chlorovanadate, is the most widely distributed vanadium mineral. Occurs as yellow to red-brown, sub-translucent, hexagonal prisms with a resinous lustre and conchoidal fracture. Streak white. H. 3; sp. gr. 7. Isomorphous with mimetite and apatite.

(*d*) *Hydrous Vanadates.*—(1) *Descloizite*, basic lead zinc orthovanadate, $(Pb,Zn)_2OH.VO_4$, occurs as orthorhombic prisms or pyramids, varying from red to dark brown in colour; greasy lustre and conchoidal fracture. Streak orange. H. 3; sp. gr. 6.

(2) *Mottramite*, basic copper lead vanadate, $(Cu,Pb)_2OH.VO_4$, dark brown to black crystalline incrustations with yellow streak. Lustre resinous; translucent.

(3) *Volborthite*, hydrous copper calcium barium vanadate, $(Cu,Ca,Ba)_2OH.VO_4$, is a green to grey mineral, with a pearly lustre and greenish-yellow streak. Occurs as tables with a perfect cleavage. H. 3·5; sp. gr. 3·5.

(4) *Brackebuschite*, hydrous lead iron manganese orthovanadate, $(Pb,Fe,Mn)_2OH.VO_4$, is a black, translucent mineral with a yellow streak.

(5) *Turanite*, basic copper vanadate, $5CuO.V_2O_5.2H_2O$, green, spongy, fibrous aggregates.

(6) *Ferganite*, hydrous uranium vanadate, sulphur-yellow scales.

(7) *Carnotite*, hydrous potassium uranyl vanadate, yellow crystalline powder or incrustations on sandstone and quartz and in the crevices of rocks.

(*e*) *Rutile* (*q.v.*, **XIII**, § I, *a*, 1) usually contains small quantities of vanadium.

§ II. **Properties and Compounds.**—(*a*) The *metal* is prepared by the reduction of the pentoxide with a mixture of rare-earth metals (" mischmetall "). It is bright silver-white, of sp. gr. 5·5 and m.p. 1730° C., is strongly attacked by nitric acid, and readily combines with nitrogen when heated, forming the mononitride, VN.

(*b*) *Vanadium pentoxide*, $V_2O_5$, is a red-brown crystalline solid melting at 658° C., but not volatile in the full heat of the Bunsen flame. It is slightly soluble in water; 1000 parts of cold water dissolve 1 part of $V_2O_5$.

(*c*) *Vanadium tetroxide*, $V_2O_4$.—Salts of this oxide are formed when the pentoxide is reduced in acid solution by mild reducing agents, *e.g.* sulphur dioxide, hydrogen sulphide, ferrous sulphate, hydrobromic, oxalic, and tartaric acids, alcohol. Their solutions are bright blue, and give a greyish-white voluminous precipitate of the hydrated oxide $V_2O_2(OH)_4.5H_2O$ with a slight excess of caustic soda; this precipitate is soluble in excess of the alkali, giving a very dark coloured solution of hypovanadate, $Na_2V_4O_9.7H_2O$.

(*d*) *Vanadium trioxide*, $V_2O_3$, gives green solutions with acids. It may be prepared as a black powder by ignition of the pentoxide in hydrogen. Its salts are prepared by reduction of acid solutions of the pentoxide with potassium iodide or magnesium.

(*e*) *Vanadium dioxide*, $V_2O_2$, forms lavender-coloured solutions with acids. Its salts are produced by reduction of the pentoxide with zinc and hydrochloric acid.

(*f*) *Vanadium monoxide*, $V_2O$, is formed by slow oxidation of the metal in air.

(*g*) *Ammonium metavanadate*, $NH_4VO_3$, is a colourless crystalline solid sparingly soluble in water, insoluble in slightly ammoniacal solutions of ammonium chloride. Yields $V_2O_5$ on ignition in air.

(*h*) *Mercurous vanadate* is formed as a flocculent white precipitate when an excess of neutral mercurous nitrate solution is added to a neutral vanadate solution. It yields $V_2O_5$ on ignition in air.

(*i*) *Lead Vanadate.*—A yellow basic salt is precipitated when a neutral lead acetate solution is added to one of sodium vanadate. Soluble in acids and concentrated caustic alkali; insoluble in, and unaffected by, alkali carbonate solution.

(*j*) *Pyrovanadic acid*, $H_4V_2O_7$, is formed when a sodium vanadate solution is boiled with strong nitric acid, as a dark red-brown flocculent precipitate resembling ferric hydroxide.

(*k*) *Ammonium Tetravanadate*, $(NH_4)_2V_4O_{11}.4H_2O$.—Crystals of this salt are deposited when acetic acid is added to a boiling solution of ammonium metavanadate until the precipitate redissolves, and the liquid is allowed to cool. The colour of the crystals is similar to that of potassium dichromate.

(*l*) *Vanadium pentasulphide*, $V_2S_5$, is not precipitated from acid solutions by hydrogen sulphide; in ammoniacal solutions the gas produces a deep brown, green, or purple colour, due to the formation of thiovanadates. The colour varies with the ammonia concentration. Upon acidification with sulphuric acid the solution gives a brown precipitate of vanadium pentasulphide, but the precipitation is rarely quantitative.

(*m*) *Tannin Complex.*—See § VII, *b*.

§ **III. Quantitative Separation.**—Recent developments in the analytical chemistry of vanadium have been less pronounced than with the majority of the rarer elements. This is due chiefly to the fact that this very reactive metal readily lends itself to oxidimetric determination, reliable methods for which have been in use for some time past. The more recent literature contains a large number of proposed volumetric processes aiming at a rapid technique by obviating the previous separation of other oxidizable elements. The practical utility of such methods lies in their application to the analysis of special steels. A survey of these new methods is beyond the scope of a manual on ore analysis, but two methods for the determination of vanadium in steel have been included in this section.

In comparison with the volumetric determination, the gravimetric separation of vanadium from other elements is a very intricate operation. The analytical technique, which has hitherto largely relied on the formation of soluble or insoluble vanadates, has been enriched by the application of the tartaric acid method and the precipitation of vanadium from tartrate (oxalate) solution by means of cupferron or tannin, or from mineral acid solution by cupferron. Vanadium is thus numbered amongst the elements recoverable from tartrate solution, and its position in the serial order of tannin precipitation has been fixed.[1]

(*a*) *From Metals of the Hydrogen-sulphide Group.*—Vanadium is not precipitated by hydrogen sulphide in acid solution, but in association with heavy metals it is liable to be coprecipitated to a certain extent. This tendency is counteracted by addition of tartaric acid to the solution (*cf.* § X, *below*).

(*b*) *From Iron, Zinc, Nickel, Cobalt, Manganese: Ammonium Sulphide Method.*—The tartaric acid filtrate from *a*, *above*, is treated as described under **XIII,** § III, *c*. 1. The precipitated sulphides are filtered off, and the filtrate treated as under *a* or *b*, § IV, *below*.

(*c*) *From Iron, Titanium, Zirconium.*—(1) *Sodium hydroxide method.* The acid solution, oxidized with a minimum of chlorate if necessary and boiled until the excess of chlorine is removed, is nearly neutralized with 10 per cent. sodium hydroxide, poured into 50 ml. of the same reagent, the mixture boiled for a few minutes and filtered, and the precipitate washed with hot water. The vanadium passes into the filtrate as sodium vanadate.

If much iron is present, the precipitate produced by sodium hydroxide should be ignited in a platinum crucible and fused with sodium carbonate, and the melt extracted with boiling water.[2] The extract is filtered through close-textured paper containing a pad of filter-pulp pressed into its apex, and the clear filtrate added to that containing the major fraction of the vanadium. The solution is treated as in § IV, *a*, *b*, or *c* for its gravimetric determination, or § V, *a* for volumetric work.

(2) *From titanium alone.*—See **XIII,** § III, *d*.

(*d*) *From Aluminium, Chromium, Uranium, Beryllium, Manganese, Zinc, Nickel.*—(1) *Cupferron method.* The cold solution is treated as described under **XIII,** § III, *e*. The precipitate is ignited to $V_2O_5$ (§ IV, *b*).

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[1] Schoeller, *op. cit.*, p. 148; *cf.* **XIII,** § III.

[2] E. Eckert, in *Ausgew. Methoden*, pp. 380, 406.

If the solution under treatment is a tartrate filtrate containing ammonium sulphide (as under *b*, *above*), it is acidified with 20 to 30 ml. of sulphuric acid (1 : 1), boiled free from hydrogen sulphide, left to cool completely, and precipitated with cupferron.

(2) *Precipitation as lead vanadate.* The solution, containing 10 ml. of nitric acid in 300 ml., is treated with a slight excess of 25 per cent. lead acetate, followed by 50 ml. of 25 per cent. ammonium acetate, solution. The precipitate is allowed to settle for two hours on a steam-bath, filtered off, washed twice with hot water, and dissolved in 5 ml. of nitric acid; the solution is diluted to 100 ml. and reprecipitated by addition of 2 to 3 ml. of lead acetate and 25 ml. of ammonium acetate solution. The precipitated lead vanadate is thoroughly washed with hot water and treated as under § IV, *e*.

(*e*) *From Phosphate.*—If vanadium preponderates, it is precipitated by cupferron (*d*, 1, *above*). It is preferable, however, whatever the relative proportions of the two elements, first to determine the vanadium volumetrically by reducing it with sulphur dioxide, etc., as explained in § V, *a*, 1. The titrated solution is boiled down to 100 ml., again reduced with sulphur dioxide, and the excess of the gas boiled off while a current of carbon dioxide is passed through the liquid. The cooled solution is treated with 20 ml. of 75 per cent. ammonium nitrate solution and 50 ml. of ammonium molybdate solution (75 g. of ammonium molybdate in 500 ml. of water, poured into 500 ml. of 1 : 1 nitric acid). The liquid is shaken, heated to 60° C., set aside for one hour (not more), and filtered. The precipitate is washed with a solution containing 50 g. of ammonium nitrate and 40 ml. of strong nitric acid per litre, dissolved in 10 ml. of 8 per cent. ammonia, and the solution (40 ml.) treated with 10 ml. of this ammonium nitrate solution and 2 to 3 ml. of the ammonium molybdate solution. The yellow phosphomolybdate is reprecipitated free from vanadium by the addition of 200 ml. of 25 per cent. nitric acid. It is dissolved in ammonia and the solution evaporated in a tared porcelain crucible (for small quantities of phosphorus); or the phosphoric acid is precipitated in the usual manner with magnesia mixture.

(*f*) *From Arsenate, Molybdate, and Tungstate.*—(1) The solution is evaporated with sulphuric acid to strong fumes to expel nitric acid, and, after cooling, water is added and the solution treated with hydrogen sulphide under pressure. The precipitate, which consists of arsenic and molybdenum sulphides and tungstic acid, is washed with acidulated hydrogen-sulphide water. The filtrate is boiled free from hydrogen sulphide, and the vanadium precipitated with cupferron. Alternatively, the filtrate may be approximately neutralized with ammonia, treated with 10 g. each of ammonium chloride and acetate, and the vanadium precipitated with tannin (§ IV, *a*).

(2) *From arsenate.* The solution is evaporated with sulphuric acid to expel nitric acid, the residue is cooled and diluted with water, and the solution is precipitated with hydrogen sulphide after addition of hydrochloric acid. Other details as under (1), *above*.

(3) *From molybdate : precipitation as manganese vanadate.*[1] The acidified solution is treated with excess of permanganate to oxidize the vanadium to

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[1] E. Gregory and W. W. Stevenson, *Chemical Analysis of Metals and Alloys*, London, 1937, p. 144.

vanadate, followed by ammonium chloride and an excess of manganous sulphate solution, and heated to boiling. Ammonia (1 : 1) is then added until the precipitation is complete. The orange precipitate is collected without delay, and washed with a hot dilute solution of ammonium chloride and ammonia. By atmospheric oxidation, both precipitate and filtrate become discoloured with brown manganic hydroxide. The precipitate is dissolved in sulphuric and sulphurous acids, the solution boiled in a flask till free from sulphur dioxide, and the vanadium titrated with permanganate (§ V, *a*).

(4) *From tungstate.* (α) See (*g*), *below.*

(β) *Cupferron method.*[1] The solution of the alkali salts is treated with 5 to 10 ml. of hydrofluoric acid, neutralized with ammonia, and acidified with 10 to 20 ml. of hydrochloric acid in a bulk of 300 ml.; the vanadium is precipitated with cupferron (§ IV, *b*), the addition of hydrofluoric acid preventing coprecipitation of the tungsten. The operation is carried out in glass vessels.

(*g*) *From Niobate, Tantalate, and Tungstate.*[2]—(1) *Vanadium preponderates: pyrosulphate-tannin-cinchonine method.* The mixed oxides are fused with potassium bisulphate in a silica crucible, and the cold melt is warmed with a 1 per cent. solution of tannin in 2·5 per cent. sulphuric acid. The contents of the crucible are transferred to a beaker with further portions of the tannin solution, and the liquid (50 to 100 ml.) is heated on the water-bath for half an hour. It is then stirred and treated with a few ml. of 2 per cent. cinchonine hydrochloride solution, which completes the flocculation of the complexes of niobium, tantalum, and tungsten. If tungsten is present the addition of cinchonine is essential for its complete precipitation. After standing cold overnight, the precipitate is collected, washed with 1 per cent. sulphuric acid containing a little tannin, and ignited to $(Ta, Nb)_2O_5$ and/or $WO_3$. The filtrate is evaporated with nitric and sulphuric acids for the destruction of the tannin, and the vanadium is determined volumetrically (§ V, *a*, 1).

(2) *Vanadium is subordinate.* The operation is conducted in two stages. In the first, the weighed mixed oxides are fused with bisulphate in a silica crucible, the melt is dissolved in 15 to 20 ml. of 20 per cent. tartaric acid solution, and the boiling liquid (100 to 150 ml.) is precipitated with 25 ml. of strong hydrochloric acid (see **XVIII,** § III, *c*, 1). The precipitated earth (tungstic) acid, which is free from vanadium, is filtered off, washed with 1 per cent. hydrochloric acid, and ignited to $(Ta,Nb)_2O_5$ $(WO_3)$.

The filtrate is neutralized with ammonia, boiled, and precipitated with 10 g. of ammonium acetate and a fresh solution of 1 g. of tannin. The bulky deep blue precipitate is collected, washed with ammonium nitrate solution, and ignited in silica. It contains the whole of the vanadium and the small balance of earth acid not precipitated by tartaric hydrolysis; tungstic acid is not quantitatively recovered by tannin and must be taken by difference.

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[1] S. G. Clarke, *Analyst*, 1927, **52**, 466, 527.

[2] Schoeller, *op. cit.*, p. 152. Unpublished tests by the senior author have shown that this method, originally worked out for the separation of vanadium from the earth acids, is applicable also to the separation of vanadium from tungsten.

In the second stage, the ignited and weighed tannin precipitate is treated by the pyrosulphate-tannin-cinchonine procedure (1, *above*).

(*h*) *From Chromate.*—The alkaline solution is neutralized with sulphuric acid, treated with 5 per cent. of its volume of sulphuric acid and a few ml. of hydrogen peroxide, and boiled until effervescence ceases, the chromate being reduced to chromic salt. The solution is cooled, and the vanadium precipitated with cupferron (§ IV, *b*).

(*i*) *From Silicate.*—For the quantitative separation of vanadium from silica, the substance must be heated in a current of dry hydrogen chloride or chlorine, vanadium volatilizing as oxychloride, which is collected in water.[1]

In the usual processes of silicate analysis, the volatilization of silica by hydrofluoric and sulphuric acids involves a risk of volatilizing part of the vanadium, if present.[2] A siliceous residue to be tested for vanadium may be treated with hydrofluoric acid, the solution evaporated nearly to dryness, and again repeatedly with hydrochloric acid to remove hydrofluoric acid (*cf.* § VIII, *b*).

(*j*) *From Aluminate.*[3]—The mixed oxides are strongly heated with six times their weight of well dried sodium carbonate in a platinum crucible for three hours over a blast-burner. The product is dissolved in 500 ml. of water, the solution boiled, and treated with solid ammonium nitrate (ten times the weight of the mixed oxides) added in small portions, care being taken not to expel the whole of the carbon dioxide by boiling. The precipitated aluminium hydroxide is collected without delay, washed with dilute ammonium nitrate solution, and ignited to $Al_2O_3$.[4] If iron is present in the mixed oxides, the above process separates it from aluminium and vanadium.

§ **IV. Gravimetric Determination.**—In metallurgical and commercial practice vanadium is usually determined volumetrically, but several gravimetric methods can be applied to vanadium solutions free from interfering elements. The tannin method is most useful for minute quantities owing to the intense blue-black colour and great bulkiness of the precipitate. Cupferron is suitable for moderate amounts (about 0·1 g.), while larger ones can be determined by one of the older methods (*c* to *f*).

In all cases the vanadium is eventually weighed as $V_2O_5$. The fusibility of the pentoxide serves as a useful indication of its purity. The pure oxide melts at 658° C.; hence if a precipitate upon ignition only sinters, or remains solid, it is not pure and requires further treatment.

(*a*) *Tannin Precipitation.*[5]—Alkaline solutions are acidified with acetic acid; acid solutions (100 to 200 ml.) are nearly neutralized with ammonia, treated with 5 to 10 g. each of ammonium chloride and acetate, heated to boiling, and precipitated with excess of tannin in freshly made solution

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[1] C. Friedheim and C. Costendyck, *Ber.*, 1900, **33**, 1611.

[2] H. Mennicke, *Die quantitativen Untersuchungsmethoden des Molybdäns, Vanadiums und Wolframs*, Berlin, 1913, p. 78; J. E. Conley, *Bull.* **212**, *U.S. Bureau of Mines*, 1923, p. 249.

[3] P. Wenger and H. Vogelson, *Helv. Chim. Acta*, 1919, **2**, 550.

[4] A check test by D. A. Lambie gave the following result: 0·1115 g. $Al_2O_3$, 0·2069 g. $V_2O_5$, and 1·9 g. $Na_2CO_3$ taken; 0·1177 g. $Al_2O_3$ found; this was pale yellow and gave positive vanadium reactions. If the recovered alumina is not perfectly white, it should be retreated.

[5] Schoeller, *op. cit.*, pp. 152, 161.

(twenty times as much tannin as the vanadium present, but not less than 0·2 g.). Tartaric acid does not prevent the precipitation of the tannin complex; oxalate solutions must be rendered slightly ammoniacal. The precipitate is allowed to flocculate, mixed with a little filter-pulp, collected on loose-textured paper, well washed with 2 per cent. ammonium nitrate solution containing a little tannin, and ignited wet in a tared porcelain crucible until the organic matter is consumed and the pentoxide fuses. The weighed oxide may be tested for silica by bisulphate fusion and solution in dilute sulphuric acid, or the solution may be titrated (§ V, *a*, 1).

(*b*) *Cupferron Precipitation.*—The cupferron precipitate obtained under § III, *d*, 1, *above* (tartaric acid does not interfere with the precipitation) is mixed with filter-pulp, collected under suction, washed with 5 per cent. sulphuric acid, and freed from wash-liquor as far as possible. It is ignited wet in a tared crucible (*cf. a, above*).

(*c*) *By Precipitation with Mercurous Nitrate.*—The feebly acid nitrate solution is treated with mercurous nitrate in slight excess, then with ammonium carbonate drop by drop until the liquor is just neutral, when it is heated to boiling and stirred until the precipitate coagulates and settles. This is collected, washed with warm water, dried, ignited gently until the paper is completely burnt away, then more strongly until the pentoxide just fuses.

(*d*) *By Precipitation as Ammonium Metavanadate.*[1]—The alkaline vanadate solution is evaporated to 50 ml., and treated with sufficient ammonium chloride to decompose the alkali salt present and give a saturated solution. This is heated on the water-bath and concentrated to 25 ml., a little ammonia being added from time to time. After standing in the cold overnight the precipitate is collected in a Gooch crucible and washed with saturated ammonium chloride solution. If too much ammonium chloride has crystallized out, it is partly redissolved by addition of dilute ammonia. The crucible is dried, heated gently to expel ammonium salts, and finally ignited at a dull red heat till the $V_2O_5$ just melts.

(*e*) *By Precipitation as Lead Vanadate.*[2]—The alkaline vanadate solution is nearly neutralized with nitric acid, a small excess of lead acetate added, and the solution heated to boiling, being stirred until the lead vanadate coagulates and settles readily. The precipitate is filtered off, washed with very dilute acetic acid, returned to the beaker, and dissolved in nitric acid. The filter-paper is ignited and the ash added to the solution, which is then evaporated with a slight excess of sulphuric acid until strong fumes are given off. The cool mass is diluted with water, the solution heated to boiling, cooled, and the lead sulphate filtered off. The filtrate is collected in a tared porcelain basin, evaporated as far as possible on the water-bath, and heated gently to drive off the sulphuric acid; the $V_2O_5$ is finally fused, allowed to cool, and weighed.

(*f*) Solutions free from other fixed constituents are evaporated with a little nitric acid in a tared porcelain basin; the residue is heated, gently at first if sulphuric acid or ammonium salts are present, then to incipient fusion, and weighed as $V_2O_5$.

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[1] F. A. Gooch and R. D. Gilbert, *Amer. J. Sci.* (4), 1902, **14**, 205.

[2] H. E. Roscoe, *J. Chem. Soc.*, 1871, **24**, 28.

§ **V. Volumetric Determination.**—The volumetric determination of vanadium is a highly specialized subject (more especially in its application to steel analysis) with a copious literature. Only a condensed account can be given here.

The great majority of the volumetric methods are oxidimetric, being based on the oxidation of a lower oxide of vanadium to the pentoxide. Amongst the oxidimetric methods, the majority rely on oxidation of the tetroxide to the pentoxide, the most commonly used oxidant being permanganate.

(*a*) *Permanganate Titration.*—In accordance with the equation:

$$5V_2O_4 + 2KMnO_4 + 3H_2SO_4 = 5V_2O_5 + K_2SO_4 + 2MnSO_4 + 3H_2O,$$

$$1 \text{ ml. of } 0{\cdot}1\text{N. permanganate} \equiv 0{\cdot}009095 \text{ g. } V_2O_5;$$

$$\equiv 0{\cdot}005095 \text{ g. V.}$$

Five reducing agents for the preliminary reduction to the tetroxide will be considered: sulphur dioxide, hydrogen sulphide, hydrochloric acid, hydrogen peroxide, and oxalic acid.

(1) *Sulphur dioxide.* The alkaline vanadate solution (400 ml.), free from nitrate, chloride, arsenate, and chromate, is acidified in a 1000-ml. conical flask with sulphuric acid (1 : 1) to give a 5 per cent. solution, and a current of sulphur dioxide is passed through the hot liquid till it becomes a pure blue: $V_2O_5 + SO_2 = V_2O_4 + SO_3$. The excess of reducing agent is boiled off while a current of carbon dioxide is conducted through the liquid. The solution is titrated at 80° C. with 0·1N. (or 0·05N.) permanganate, the colour changing from blue through green to pale yellow (or colourless, if but little vanadium is present), until finally the characteristic pink tinge of the permanganate appears. The permanganate is standardized against sodium oxalate. Conversion factor for $Na_2C_2O_4$ to $V_2O_5$ : 1·3575.

If it is considered advisable to obtain a confirmatory reading, the hot titrated solution is once more reduced with sulphur dioxide, and again titrated after having been freed from sulphur dioxide.

(2) *Hydrogen sulphide* is useful for removing arsenic, etc. from the solution; the filtrate is freed from hydrogen sulphide by boiling. Titration of the hot liquid with permanganate, however, gives a slightly high result, which is ascribed to the formation of polythionic acids.[1] If hydrogen sulphide has been used, the correct procedure is as follows:

The hot solution freed from hydrogen sulphide is titrated with permanganate as under (1), *above*. The reading is noted as a guide. The hot solution is then treated with a decided excess of permanganate to a permanent deep mauve and allowed to stand, overnight if convenient. It is then treated with sulphur dioxide, etc. as under (1). The lower reading obtained in the second titration is taken as correct.

(3) *Hydrochloric acid.*[2] When a solution of vanadate is boiled with hydrochloric acid, reduction to the tetroxide takes place:

$$V_2O_5 + 2HCl = V_2O_4 + H_2O + Cl_2.$$

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[1] G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1921, **43**, 1566.

[2] E. Campagne, *Compt. rend.*, 1903, **137**, 570; A. H. Low, *Technical Methods of Ore Analysis*, 10th edition, p. 251.

As hydrochloric acid has no action on ferric salt, this procedure obviates the separation of vanadium from iron, a great advantage in metallurgical analysis; but the above reaction is reversible to a certain extent, and complicated by other elements which may be present. The process should be used only in routine work on material the composition of which is known to the operator, and not rich in vanadium. For work of the highest accuracy, sulphur dioxide reduction must be applied.

The vanadium solution is boiled down with 40 ml. of sulphuric acid (1 : 1) until heavy white fumes are given off. The cold acid is diluted, and the solution treated with excess of solid permanganate to ensure the complete oxidation of iron and organic matter. The solution is then boiled down with 50 ml. of strong hydrochloric acid to incipient evolution of white fumes, and again a second time, after addition of 25 ml. of strong hydrochloric acid, until the white fumes escape freely. The acid is then diluted with 200 ml. of water, and the solution titrated at 80° C. with permanganate.

Vanadium and iron may be determined in the same solution by the following combination process: The feebly acid sulphate solution is reduced with sulphur dioxide and the excess of the gas expelled by boiling in a current of carbon dioxide (1, *above*). The solution is titrated, first cold, then at 80° C., with permanganate, the ferrous and vanadyl sulphates being oxidized. The titrated solution is then treated with more sulphuric acid, boiled down twice in succession with hydrochloric acid, and titrated, as in the preceding paragraph. The permanganate consumed in the second titration gives the amount of vanadium, and the difference between the first and second titration the iron.

(4) *Hydrogen peroxide.*[1] This reagent reduces vanadic acid in presence of strong sulphuric acid. The solution is heated with 10 to 20 ml. of the latter acid until heavy white fumes are evolved. The mass is cooled, a little powdered permanganate added, and the heating repeated. When quite cold, the acid is decolorized by dropwise addition of hydrogen peroxide, and allowed to cool. Finally, 1 ml. of hydrogen peroxide is added drop by drop during agitation, the excess of reagent being decomposed by the vanadyl sulphate. After 10 to 15 minutes, the acid is diluted to 300 ml., and the solution titrated at 70° C. with permanganate.

(5) *Oxalic acid.*[2] The solution is treated with 30 ml. of strong sulphuric acid and 0·2 g. of oxalic acid, and evaporated to fumes in an atmosphere of carbon dioxide. After cooling, 500 ml. of water is added, and the hot solution titrated as before.

(*b*) *Iodimetric Titration.*—(1) *Liberation of bromine from potassium bromide.*[3] The solution of alkaline vanadate containing not more than 0·3 g. of $V_2O_5$ is distilled with 1·5 to 2 g. of potassium bromide and 30 ml. of strong hydrochloric acid, bromine being liberated:

$$V_2O_5 + 2HBr = V_2O_4 + H_2O + Br_2.$$

The bromine is distilled over into a 10 per cent. solution of potassium iodide, and the iodine set free is titrated with 0·1N. thiosulphate (1 ml. ≡ 0·009095 g. $V_2O_5$). This method, although requiring a certain amount of apparatus, is quicker than the permanganate methods, and is exceedingly accurate.

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[1] J. R. Cain and J. C. Hostetter, *J. Ind. Eng. Chem.*, 1912, **4**, 250; A. W. Hothersall, *J. Soc. Chem. Ind.*, 1924, **43**, 270 T.

[2] H. Mennicke, *op. cit.*, p. 60.

[3] F. A. Gooch and J. S. Curtis, *Amer. J. Sci.* (4), 1904, **17**, 43.

(2) *Direct titration.*[1] In this process, the acid vanadate solution liberates iodine from potassium iodide according to the equation:

$$V_2O_5 + 2HI = V_2O_4 + H_2O + I_2.$$

As quinquevalent vanadium catalytically induces oxidation of the iodide by atmospheric oxygen, the determination must be carried out with exclusion of air.

The 0·1N. vanadate solution is acidified with 5 ml. of 6N. sulphuric acid and boiled in a current of carbon dioxide in a conical flask provided with inlet and outlet tubes, the former reaching to within 1 cm. of the surface of the solution, the latter leading into a water-trap. When all the air has been expelled the flask is allowed to cool to room temperature while the gas continues to bubble through the trap. Solid potassium iodide (2 to 4 g.) is rapidly added, the stopper being removed for a moment. The solution is shaken for 2 minutes, diluted to 300 ml., and the iodine titrated with 0·1N. thiosulphate, starch being added towards the end.

(*c*) *Ferrous Sulphate Titration.*[2]—The process is based on the reaction:

$$V_2O_5 + 2FeSO_4 + H_2SO_4 = V_2O_4 + Fe_2(SO_4)_3 + H_2O.$$

The solution is acidified with sulphuric acid to 6N. concentration, and treated with excess of permanganate. The purple colour is just discharged with 0·1N. ferrous or ferrous ammonium sulphate. Phosphoric acid is added to discharge any colour due to ferric salt, a few drops of a one per cent. solution of diphenylamine in strong sulphuric acid are added, and the liquid is titrated with the ferrous salt solution till the blue colour disappears. Potassium ferricyanide may also be used as an internal or external indicator, the end-point being shown by the appearance of a blue colour. Clark [3] adds an excess of ferrous salt solution, and measures the excess by titration with 0·1N. dichromate.

§ **VI. Colorimetric Determination.**[4]—Hydrogen peroxide gives with acidified vanadate solutions a brownish-red colour which is bleached by excess of peroxide. The coloured compound is not pervanadic acid, but a peroxidized sulphate, which reacts with more peroxide, yielding light yellow orthoperoxyvanadic acid. Increase in the sulphuric acid concentration restores the reddish-brown colour. A considerable excess of acid is therefore required, and a minimum excess of hydrogen peroxide over the ratio $V : H_2O_2 = 1$.

The substance to be tested is fused with sodium carbonate and nitrate, and the mass dissolved in dilute sulphuric acid; the solution should contain 20 per cent. of free sulphuric acid. After some minutes' standing, it is cautiously treated with 3 per cent. hydrogen peroxide one drop at a time until the colour no longer deepens (one drop of 3 per cent. hydrogen peroxide suffices for very small quantities of vanadium). The tint is compared with that produced by a standard vanadium solution under the same conditions as those of the assay.

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[1] J. B. Ramsay, *J. Amer. Chem. Soc.*, 1927, **49**, 1138; A. D. Mitchell and A. M. Ward, *Modern Methods in Quantitative Chemical Analysis*, London, 1932, p. 162.

[2] C. M. Johnson, *Chemical Analysis of Special Steels*, 1920, p. 6; N. H. Furman, *Ind. Eng. Chem.*, 1925, **17**, 314; A. S. Russell, *J. Soc. Chem. Ind.*, 1926, **45**, 571.

[3] W. W. Clark, *Met. Chem. Eng.*, 1913, **11**, 91.

[4] J. Meyer and A. Pawletta, *Zeitsch. anal. Chem.*, 1926, **69**, 15.

The standard is prepared by dissolving 1·286 g. of ammonium metavanadate in 10 per cent. sulphuric acid and diluting to one litre: 1 ml.≡0·0010 g. $V_2O_5$.

Titanium interferes with the above process, but the colour due to pertitanic acid is bleached by hydrofluoric acid, whereas the vanadium compound is unaffected. If the carbonate melt of the mineral is extracted with water and the extract filtered prior to acidification (*above*), any titania present will remain in the insoluble residue.

§ **VII. Detection in Minerals.**—The fine powder is fused with five times its weight of sodium carbonate and nitrate or peroxide, and the melt is leached with hot water. The filtered solution is nearly neutralized with nitric acid, evaporated to dryness, and the residue extracted with hot water. The filtered extract is used for some of the following tests:

(*a*) Boiling with a slight excess of acetic acid produces an orange coloration (tetravanadate).

(*b*) The boiling acid solution obtained under (*a*) is treated with ammonium chloride and a freshly prepared solution of tannin: a voluminous flocculent blue-black precipitate is obtained.[1] The vanadium-tannin complex has intense colouring power, and we consider this reaction the most sensitive test for vanadium. It often detects vanadium in presence of large quantities of other elements giving colourless tannin precipitates: a trace of vanadium imparts a pale blue colour to the aluminium-tannin complex.

(*c*) Boiling with a large excess of nitric acid produces a deep red-brown flocculent precipitate of pyrovanadic acid.

(*d*) Evaporation of the solution with hydrochloric acid to destroy nitrates finally gives a blue solution of vanadyl chloride; potassium bromide brings this about more readily, bromine being liberated. Reducing agents (sulphur dioxide, hydrogen sulphide, alcohol, oxalic or tartaric acid, ferrous sulphate) act similarly to potassium bromide.

(*e*) The solution, treated with one-fifth of its volume of sulphuric acid, gives an intense red-brown colour upon dropwise addition of hydrogen peroxide (*cf.* § VI, *above*). This is a very sensitive test.

(*f*) Saturation of the solution with solid ammonium chloride causes quantitative precipitation of ammonium metavanadate, which is converted into vanadium pentoxide upon ignition (*cf.* § IV, *d*).

(*g*) Lead acetate gives a pale yellow precipitate in the cold in solutions slightly acidified with acetic acid; the precipitate is soluble in nitric acid.

(*h*) The acidified solution, when treated with excess of ammonia and saturated with hydrogen sulphide, gradually turns cherry-red to violet-red. This reaction is very delicate, but molybdate gives a similar colour.

§ **VIII. Determination in Ores and Alloys.**—(*a*) *General Method for Ores Low in Silica.*—(1) *Peroxide fusion.* 0·5 to 1 g. of ore is mixed with three times its weight of sodium peroxide in a nickel crucible; the mixture is covered with 1 g. of the peroxide, and heated until it sinters together and has a uniform black appearance (fusion is unnecessary and objectionable). The cold mass is leached with hot water, and the solution heated to boiling and saturated with carbon dioxide. The precipitate is allowed to settle, filtered off, and washed with a 2 per cent. solution of sodium carbonate. The filtrate is just acidified with nitric acid, and boiled free from carbon dioxide, and an excess of 10 per cent. lead acetate solution is added, followed by 3 to 4 g. of ammonium acetate, whereby all the vanadium is precipitated as lead vanadate, together with chromate, tungstate, molybdate, phosphate, and arsenate, if present.

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[1] C. Matignon, *Compt. rend.*, 1904, **138**, 82.

The precipitate is dissolved by boiling with a few ml. of nitric acid, an excess of dilute sulphuric acid is added, and the whole evaporated to strong fumes. Molybdenum, arsenic, and lead are removed from the diluted solution by hydrogen sulphide under pressure, the tungsten being found as tungstic acid in the sulphide precipitate. If chromium is absent, the filtrate from the sulphides is boiled to expel hydrogen sulphide and titrated at 70° to 80° C. with 0·05N. permanganate; the solution is then reduced with sulphur dioxide, the excess boiled off, and the permanganate titration repeated. The last figure is taken as correct.

If chromium is present, the filtrate from the sulphides is boiled till free from hydrogen sulphide, and precipitated below 20° C. with cupferron after liberal addition of filter-pulp. The precipitate is collected, washed, and compressed by suction, ignited in a tared silica crucible, and weighed as $V_2O_5$. This figure serves as a guide, the final result being obtained by titration. To this end the weighed precipitate is fused with bisulphate, the melt dissolved in hot dilute sulphuric acid, and the solution transferred to a flask and reduced with sulphur dioxide, etc., as in § V, *a*, 1.

(2) *Carbonate-nitrate fusion.* 0·5 to 1 g. of the finely powdered ore is fused with six times its weight of a mixture of equal parts of sodium carbonate and potassium nitrate in a platinum crucible. The cold melt is extracted with hot water, and the solution filtered; the residue is washed with hot water, ignited, and again fused with the same mixture. The combined filtered extracts are nearly neutralized with nitric acid and evaporated to dryness (a blank test should be run to ascertain the amount of acid necessary, as an excess would lead to reduction of vanadate by the nitrite present). The residue is taken up with hot water, the solution filtered and treated with an excess of lead acetate, and the precipitate of lead vanadate treated as under (1), *above*.

(*b*) *General Method for Ores Rich in Silica: Acid Attack.*—One to 5 g. of ore is digested with *aqua regia* until completely attacked; the liquid is evaporated to dryness, the residue boiled with hydrochloric acid (1 : 1) until all soluble matter dissolves, and the liquor filtered from the siliceous residue, which may still contain some vanadium: the residue is ignited in platinum, and evaporated nearly to dryness (twice) with hydrofluoric acid, then twice with hydrochloric acid to expel the fluorine compounds. The residue is taken up with dilute hydrochloric acid and the filtered liquid added to the main solution, which is then saturated with hydrogen sulphide to remove heavy metals. The filtrate from the sulphides is boiled free from hydrogen sulphide, oxidized with nitric acid, neutralized, and poured into a solution of 6 g. of sodium hydroxide in 100 ml. of boiling water. The precipitate is mixed with filter-pulp, collected, washed with hot water, ignited in a platinum crucible, and fused with sodium carbonate. The melt is extracted with hot water, and the solution filtered. The filtrate is added to that obtained in the caustic soda treatment, saturated with carbon dioxide, filtered if necessary, neutralized with nitric acid, and precipitated with lead acetate solution, etc., as under *a*, 1, *above*.

(*c*) *Shorter Volumetric Method for Pure Ores and Ferrovanadium.*[1]—0·5 g. to 1 g. of ore (0·25 g. of ferrovanadium) is dissolved in dilute nitric acid, and the solution is evaporated with sulphuric acid until all the nitric acid and part of the sulphuric acid are expelled. The residual mass is taken up in hot water, and lead sulphate filtered off if present. If this is yellowish instead of white, it should be boiled with hydrochloric acid and once more evaporated with sulphuric acid, the filtrate from the reprecipitated lead sulphate being added to the first.[2]

The solution or filtrate is boiled with a little hydrochloric acid and 10 ml. of sulphurous acid until the sulphur dioxide is eliminated; it is then saturated with hydrogen sulphide, the precipitate collected and washed as usual, and the filtrate boiled, oxidized with a minimum of potassium chlorate, and evaporated to incipient fuming for the removal of hydrochloric acid. The cold acid is diluted with hot water and the solution treated with excess of sodium hydroxide; the filtrate is reserved, and the washed precipitate ignited and fused with sodium carbonate, etc., as under *b*, *above*.

The combined filtrates from the sodium hydroxide and carbonate treatments are neutralized with sulphuric acid in a 1000-ml. conical flask, and an excess of 20 ml. of strong sulphuric acid is added. The solution (500 ml.) is boiled, treated with a decided excess of permanganate, and set aside overnight.

Next day the solution is treated with 20 to 30 ml. of freshly prepared sulphurous acid, and boiled for an hour with a steady stream of pure carbon dioxide passing through it. It is titrated at 70° C. with permanganate.

(*d*) *Determination of Vanadium* (*and Chromium*) *in Iron Ores and Rocks.*[3]—Five g. of the fine powder is fused with 20 g. of sodium carbonate and 3 g. of potassium nitrate in platinum over a blast-burner. The cold melt is extracted with hot water, a few drops of alcohol are added to decompose manganate, and the solution is filtered; if much vanadium is present, the residue is ignited and again fused with the above mixture. The combined filtrates are *nearly* neutralized with nitric acid (quantity required ascertained by a blank test) and evaporated to dryness; the residue is taken up with hot water, and the solution filtered. The insoluble fraction contains silica, alumina, and part of the chromium; should determination of the latter be required, the residue is ignited, evaporated to dryness with hydrofluoric and sulphuric acids, ignited, and fused with soda and nitre, the filtered extract being added to the main solution.

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[1] E. Eckert, in *Ausgew. Methoden*, pp. 380, 406.

[2] We are applying bisulphate fusion for the decomposition of some vanadium ores, dissolving the melt in hot dilute sulphuric acid. The procedure results in a great saving of time.

[3] W. F. Hillebrand, *J. Amer. Chem. Soc.*, 1898, **20**, 209.

The cold, slightly alkaline solution is treated with an excess of a saturated neutral solution of mercurous nitrate, heated to boiling, and filtered; the precipitate is washed with hot 1 per cent. ammonium nitrate solution, dried, and ignited at low temperature in platinum. The residue is fused with sodium carbonate, the melt is extracted with water (the chromium being determined colorimetrically as neutral chromate if required), and the solution acidified with sulphuric acid and saturated with hydrogen sulphide under pressure. The filtrate from the sulphides is boiled to expel hydrogen sulphide in a current of carbon dioxide, and the hot solution is titrated with 0·05N. permanganate. The solution should be once more reduced, this time with sulphur dioxide, the excess expelled by boiling, and the solution titrated at 80° C. with permanganate. The mean of the two readings gives the correct result. If more than 5 mg. of chromium is present, a blank test should be made with the same quantity of pure chromate, which is reduced as *above* with sulphur dioxide, and the hot solution titrated.

(*e*) *Determination in Carnotite.*—See **XXII,** § VIII, *c*.

(*f*) *Determination in Steel.*—(1) *Chromium is absent.*[1] The steel (2·5 to 5 g.) is dissolved in nitric acid (1 : 1), and the solution evaporated to dryness in a porcelain casserole. The residue is baked until the nitrates have been decomposed, cooled, and dissolved in strong hydrochloric acid. The bulk of the iron is eliminated by double ether extraction, the ethereal fraction being shaken with a little strong hydrochloric acid which, after settling, is added to the aqueous solution. This is freed from ether by double evaporation with hydrochloric acid, the vanadium being converted into vanadyl chloride. The residue is dissolved in hydrochloric acid, and the solution evaporated with 5 to 10 ml. of sulphuric acid until white fumes are evolved. The cold acid is diluted with 100 to 200 ml. of water and titrated at 70° C. with 0·02N. permanganate (§ V, *a*, 3).

(2) *Chromium and tungsten are present.*[2] The weighed sample (2 g. for less than 1 per cent., 1 g. for 1 to 2 per cent., 0·5 g. for more than 2 per cent., vanadium) is digested in a 300-ml. flask with 40 ml. of sulphuric acid (1 : 4) on a hot-plate until vigorous action ceases, when 1 to 4 ml. of hydrofluoric acid (according to the amount of tungsten present) is added to complete dissolution. The solution is oxidized with 2 to 3 ml. of strong nitric acid, boiled, diluted to 100 ml., treated with 1 g. of ammonium persulphate, boiled for 5 minutes, and removed from the heat.

The solution is treated with 0·1N. ferrous ammonium sulphate until chromate and vanadate are completely reduced (as shown by the disappearance of the yellow colour), then with another 5 ml. of the same solution, and cooled. The vanadium alone is re-oxidized by addition of 0·1N. permanganate until a permanent pink colour is produced. The excess of permanganate is next reduced by the cautious addition of 5 per cent. sodium nitrite solution, care being taken not to add more than 5 drops in excess, which is destroyed by addition of 2 g. of urea. After standing for 5 minutes the solution is treated with 5 ml. of hydrofluoric acid and 10 drops of indicator (*below*), and set aside for a short time to allow the purple colour to develop. The solution is then titrated with N./51 ferrous ammonium sulphate solution until one drop causes the colour to change to green.

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[1] E. Campagne, *Ber.*, 1903, **36**, 3166.

[2] *Standard Methods of Analysis of Iron, Steel, and Ferro-alloys*, published by the United Steel Companies, Ltd., Sheffield; revi[illegible] and enlarged edition, 1936, p. 39.

The N./51 ferrous ammonium sulphate solution is prepared from about 7·9 g. of the salt dissolved in 120 ml. of dilute sulphuric acid (1 : 5 water) and diluted to one litre, and standardized against 10 ml. of 0·05N. permanganate in presence of the indicator.

The indicator is prepared from 100 ml. of 0·01M. sodium diphenylamine-sulphonate solution, 5 ml. of concentrated sulphuric acid, and 200 ml. of water. The liquid is slowly treated during constant agitation with 0·1N. dichromate solution until the colour definitely changes from blue to purple; an excess of 8 ml. of dichromate solution is then added, and the solution stirred and cautiously titrated with 0·1N. ferrous ammonium sulphate until one drop produces a deep green colour. The mixture is then transferred to a cylinder, and set aside for 3 to 4 days until a portion of the supernatant liquid gives no colour with a mixture of 100 ml. of water, 2 ml. of the dichromate, and 5 ml. of strong sulphuric acid. The liquid is cautiously siphoned off, and the deposit stirred up with 300 ml. of water and 15 ml. of strong sulphuric acid. When the deposit has settled completely, the clear liquid is again siphoned off; the deposit is shaken up with 100 ml. of water, the suspension being used as the indicator. The precipitate does not settle readily and requires only occasional shaking.

**§ IX. Determination of Impurities in Ores and Ferrovanadium.**—The most objectionable impurities are those which form soluble sodium salts on fusion with sodium carbonate, *i.e.* phosphorus and arsenic. Molybdenum and chromium are not so objectionable, as in most steels to which vanadium is added these elements are also present. The impurities met with in ferrovanadium are silicon, phosphorus, sulphur, manganese, arsenic, nickel, and carbon.

(*a*) *Silicon and Phosphorus.*[1]—Two to 5 g. of crushed material is decomposed with nitric acid (1 : 1); the solution is taken to dryness, and the residue baked until nitrates are decomposed. The cold mass is dissolved in hydrochloric acid, the solution again evaporated, the residue dehydrated at 130° C., once more dissolved in hydrochloric acid, and the solution filtered. The insoluble matter is treated for silica as usual. In the case of ferrovanadium, the quantity found is calculated to silicon.

The filtrate from the silica is freed from excess acid by evaporation, part of the vanadium being reduced to vanadyl salt. The reduction is completed by addition of ferrous sulphate, and the phosphoric acid in the solution is precipitated with molybdate mixture.

(*b*) *Sulphur.*—Decomposition is effected with *aqua regia.* After evaporation to dryness, followed by double evaporation with hydrochloric acid, the residue is dissolved in hydrochloric acid, the excess of which is evaporated, the solution diluted with water, and the insoluble filtered off. The filtrate is precipitated with barium chloride.

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[1] *Ausgew. Methoden*, p. 409.

(*c*) *Manganese.*[1]—The filtrate from the silica, obtained as under (*a*), is precipitated hot with 10 per cent. sodium hydroxide solution and a little sodium peroxide. The precipitate is collected, washed, dissolved in hydrochloric acid, and the precipitation repeated. The precipitate is dissolved in hydrochloric acid, and the iron separated from manganese by zinc oxide.

(*d*) *Arsenic.*—The material is attacked with nitric acid, and evaporated with 10 ml. of strong sulphuric acid until white fumes are evolved. After dilution, silica, lead sulphate, etc. are filtered off, the filtrate is reduced with sulphur dioxide, the excess of the latter boiled off, and the arsenic, etc. precipitated with hydrogen sulphide. The precipitate is extracted with sodium sulphide, the solution containing the arsenic evaporated to fumes with strong sulphuric acid, diluted with 25 ml. of water and 50 ml. of strong hydrochloric acid, and precipitated with hydrogen sulphide. The arsenic sulphide is boiled with sulphuric acid and titrated as usual with iodine.

(*e*) *Nickel.*—The solution, freed from silica as under (*a*), is evaporated to small bulk, diluted, treated with tartaric acid, made ammoniacal, and slightly acidified with acetic acid; the nickel is then precipitated with dimethylglyoxime.

(*f*) *Carbon:*[2] *Combustion Method.*—One to 2 g. of finely powdered ferrovanadium is heated in an electric tube-furnace at 1200° C. in oxygen, the carbon dioxide being absorbed and determined as usual. If the material is very high in vanadium, the powder should be mixed with pure copper oxide to prevent sintering and creeping.

§ **X. Complete Analysis of Ores.**—Ores consisting of vanadates of heavy metals (*e.g.* vanadinite, descloizite, mottramite, pucherite) are usually found associated with lead and zinc minerals. The determination of the metals should be carried out by the tartaric acid method, which obviates coprecipitation of vanadium with the sulphides of the heavy metals in the form of thiovanadates.[3]

*First Portion.*—The ore (1 g.) is decomposed by *aqua regia*, and the solution evaporated with 8 ml. of sulphuric acid to incipient evolution of white fumes. The acid is cooled, the sides of the beaker are rinsed down with water, and the evaporation is repeated as before. The cold mass is treated with 40 ml. of water, and the solution digested on a steam-bath and set aside overnight.

The insoluble fraction (lead sulphate and gangue) is filtered off and analysed in known manner. The filtrate is treated with 4 g. of tartaric acid, reduced with sulphur dioxide, boiled to expel excess, and saturated with hydrogen sulphide. The precipitate is tested for copper, bismuth, arsenic, and molybdenum. The filtrate from the sulphides is treated with ammonium chloride, ammonia, and more hydrogen sulphide to precipitate iron, zinc, nickel, and manganese.[4]

The filtrate from the last sulphide precipitate is evaporated with 50 ml. of nitric acid and 10 ml. of sulphuric acid for the destruction of the tartaric acid. The cold acid is diluted with 250 ml. of water, an excess of permanganate is added, and the solution set aside overnight (§ V, *a*, 2). The solution is then reduced with sulphur dioxide, the excess of the gas boiled off, and the vanadium titrated with permanganate.

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[1] *Ausgew. Methoden*, p. 410.
[2] *Ibid.*, p. 409.
[3] M. H. Hey, *Min. Mag.*, 1933, **23**, 385.
[4] Precipitation of manganese sulphide: *cf.* XIII, § III, *c*, 1.

*Second Portion: Sulphur.*—See § IX, *b*.

*Third Portion: Phosphorus.*—See § IX, *a*.

*Fourth Portion: Chlorine.*—One g. of ore is digested with dilute nitric acid below 50° C. until decomposed. The solution is diluted and filtered, and the filtrate precipitated with silver nitrate.

*Fifth Portion.*—Combined water is determined by Penfield's method.

## XVIII.—NIOBIUM AND TANTALUM.

§ **I. Minerals.**—Niobium and tantalum occur always in association, the pentoxides replacing each other in their minerals.

(*a*) *Tantaloniobates.*—(1) *Columbite-Tantalite.* Strictly speaking, these two minerals are varieties of the same species, orthorhombic iron manganese tantaloniobate $(Fe,Mn)O.(Nb,Ta)_2O_5$, which forms an isomorphous series in which niobium and tantalum replace each other in all proportions. The minerals in which niobium preponderates are called columbite, while the term tantalite is reserved for those containing over 50 per cent. of $Ta_2O_5$. The ferrous and manganous oxides likewise are vicarious, and this replacement gives rise to another isomorphous series, the members of which are defined by the prefixes "ferro-" and "mangano-", according to the preponderance of one or the other oxide. Four varieties may therefore be distinguished:

*ferrocolumbite* — *ferrotantalite*
*manganocolumbite* — *manganotantalite.*

This distinction has a certain practical importance, since the varieties rich in iron show greater magnetic susceptibility than those rich in manganese.

The specific gravity increases with the tantalum content from 5·3 (substantially pure niobate) to 8. H. 6. Occurs crystallized (lustrous prismatic crystals showing longitudinal striations) or massive. Colour iron-black to brownish-black; streak dark brown to reddish-brown. The only ore of commercial importance.

(2) *Microlite*, calcium tantalate, $2CaO.(Ta,Nb)_2O_5$; pale yellow to brown; cubic.

(3) *Stibiotantalite*, antimony tantalate, $Sb_2O_3.(Ta,Nb)_2O_5$; various shades of yellow; orthorhombic.

(4) *Bismuthotantalite*, bismuth tantalate, $Bi_2O_3.(Ta,Nb)_2O_5$; orthorhombic.

(5) *Samarskite-Yttrotantalite*, orthorhombic tantaloniobates of yttrium, calcium, iron, and uranium, samarskite containing more niobic, yttrotantalite more tantalic, oxide. Yellow to black.

(6) *Fergusonite*, an yttrium tantaloniobate containing uranium and calcium. Tetragonal; brownish-black.

(*b*) *Titanoniobates.*—These rare and complex minerals of uncertain composition contain titania as an essential constituent along with niobic and tantalic oxides, as well as rare (usually yttria) earths. The better known are:

(1) *Aeschynite*, a titanoniobate of ceria earths, thoria, lime, and iron.

(2) *Euxenite-Polycrase*, titanoniobates of yttria earths, uranium, lime, and iron. Orthorhombic; black.

(3) *Blomstrandine* and *priorite* are chemically and crystallographically related to the two preceding.

(4) *Betafite*, rich in uranium, occurs in large yellow octahedra.

(*c*) *Other Minerals.*—(1) *Strüverite-Ilmenorutile*, tetragonal, isomorphous, are related to rutile; they contain ferrous tantaloniobate in combination with titania, strüverite being richer in tantalum than ilmenorutile.

(2) *Tantalocassiterite*, tetragonal, is cassiterite containing subordinate amounts of tantalic oxide.

(3) A number of rare zirconium silicates (see **XIV**, § I, *b*) contain small quantities of earth acid.

§ **II. Properties and Compounds.**—(*a*) The *elements* are obtained by electrolysis, or reduction with sodium, of the fused double fluorides (*f*, *below*). They are light grey, malleable and ductile metals, insoluble in *aqua regia*, but readily soluble in a mixture of hydrofluoric and nitric acids. When heated they combine with oxygen, nitrogen, and hydrogen, forming the oxides, nitrides, and hydrides, respectively. Sp. gr. 8·3 (Nb), 17 (Ta); m.p. 1800° C. (Nb), 2850° C. (Ta).

(*b*) The *pentoxides*, $Nb_2O_5$ (sp. gr. 4·55) and $Ta_2O_5$ (sp. gr. 8·71), are white, infusible, and amorphous. Niobic oxide turns light yellow when heated, while tantalic oxide remains white. They are soluble in hot strong hydrofluoric acid, and in molten alkali pyrosulphate, carbonate, or hydroxide. When extracted with hot water or dilute acids, the pyrosulphate melt leaves an insoluble residue of earth acid; extraction with tartaric or oxalic acid, however, results in a clear solution of the tartaro- or oxalo-earth acids. The melt obtained by fusion with potassium carbonate or hydroxide dissolves in water, giving a solution of potassium niobate or tantalate. On the other hand, the melt resulting from fusion with sodium carbonate or hydroxide, when treated with water, gives a residue of insoluble sodium niobate or tantalate.

(*c*) The *hydrated earth acids*, $Nb_2O_5.xH_2O$ and $Ta_2O_5.xH_2O$, are obtained as white precipitates when: (1) solutions of the potassium salts are acidified with mineral acids; (2) solutions of the oxalo-acids are treated with excess of ammonia; (3) the bisulphate melt of the oxides is leached with water; or (4) soluble niobium or tantalum compounds decompose hydrolytically. The precipitates do not dissolve in alkalis or acids, with the exception of hydrofluoric acid. On ignition, they are converted into the pentoxides.

(*d*) *Potassium Salts.*—*Potassium niobate*, $4K_2O.3Nb_2O_5.16H_2O$, isomorphous with the *tantalate*, $4K_2O.3Ta_2O_5.16H_2O$. Readily soluble in water, the tantalate showing a much greater tendency to hydrolyse than the niobate.

(*e*) *Sodium Salts.*—The *niobate*, $7Na_2O.6Nb_2O_5$, and the *tantalate*, $4Na_2O.3Ta_2O_5$, are obtained either by fusion (*b*, *above*), or by saturation of the solution of the potassium salts with solid sodium chloride. White pulverulent precipitates, sparingly soluble in water, insoluble in solutions of high sodium-ion concentration.

(*f*) *Double Fluorides.*—The solution of the earth acids in hydrofluoric acid contains the pentafluorides, which yield double salts with potassium fluoride. *Potassium fluorotantalate*, $K_2TaF_7$, soluble in 200 parts of cold dilute hydrofluoric acid, may be obtained as a crystalline precipitate (orthorhombic needles) by treatment of concentrated tantalum fluoride solutions with potassium fluoride. The corresponding niobium salt, however, is very soluble in dilute hydrofluoric acid, and is decomposed by water with formation of the *oxyfluoride*, $K_2NbOF_5$, thin monoclinic plates soluble in 12·5 parts of water. Marignac's classic separation process (still applied in the extraction of the two metals from their ores) is based on the different solubilities of the complex fluorides.

(*g*) *Tannin Complexes.*—These are obtained as voluminous flocculent precipitates when the neutralized hot solutions of the tartaro- or oxalo-acids are treated with ammonium chloride and excess of tannin solution. The tantalum complex, which is sulphur-yellow, is precipitated at a higher acid concentration than the vermilion-red niobium complex. In oxalate solutions the interval between the precipitation of the two compounds is sufficiently marked to permit the quantitative separation of the two elements (§ III, *i*). The tannin complexes are insoluble in dilute mineral acids. On ignition they are converted into the pentoxides.

**§ III. Quantitative Separation.** — *Definitions.* — The time-honoured generic term "earth acids" is used in this section to denote niobic and tantalic oxides, anhydrous or hydrated; it does not include titanic or tungstic acid. The term "pentoxides" as used here refers to $Nb_2O_5$ and $Ta_2O_5$.

As mentioned in the Preface, the analytical chemistry of niobium and tantalum has been completely revolutionized since the appearance of the first edition of this work, and brought into line with that of the commoner elements, so that an experienced operator can now analyse complex materials containing these elements as a matter of routine and with a precision which, only a few years ago, was regarded as unattainable.

The difficulty of obtaining stable soluble niobium and tantalum compounds has been the chief cause of the uncertainties and complications of earth-acid analysis. This has been overcome by recourse to the soluble organic complexes of the earth acids, but the problem of recovering the dissolved elements from such solutions has had to be solved. That search led to the discovery of the peculiar action of tannin upon solutions of the organic complexes of the earth acids and a number of elements; thanks to this reaction, tannin has become the paramount reagent in this branch of mineral analysis. The older analytical processes, involving the manipulation of intractable complex hydrolysis precipitates, have been rendered obsolete by the new methods described *below*.[1]

(*a*) *From Silica*[2] *and Stannic Oxide.*[3]—(1) *The earth acids preponderate.*

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[1] All the methods given in this section have been described in our 33 papers published in the *Analyst* (1922–1936). The published data were subsequently re-arranged and systematically presented in the monograph entitled *The Analytical Chemistry of Tantalum and Niobium*, by W. R. Schoeller (London, 1937), which should be regarded as the final *exposé* of our methods. Chapter XVI of that work reproduces the summaries of all our papers.

[2] W. R. Schoeller and A. R. Powell, *Analyst*, 1928, **53**, 258.

[3] W. R. Schoeller and H. W. Webb, *ibid.*, 1931, **56**, 795.

The mixture of oxides, or the mineral, is fused with potassium bisulphate in a silica crucible. When cold, the crucible is filled with 15 to 20 ml. of 20 per cent. tartaric acid solution and warmed over a very small flame until the melt becomes detached. The contents of the crucible are transferred to a squat 250-ml. beaker with 50 to 80 ml. of warm distilled water and 5 ml. of 10 per cent. sulphuric acid, and the particles of the melt disintegrated with a stout glass rod, leaving a pulverulent residue. The beaker is then warmed over a small flame while the liquid is being continuously stirred: the glass rod is given a circular movement alternating with a criss-cross motion across the centre of the beaker. This agitation serves to keep the whole of the precipitate in constant motion, when solution takes place readily as the temperature nears the boiling-point. Should any of the precipitate adhere to the bottom of the beaker it usually leaves a residue of semi-transparent flakes of earth acid, which must be collected, washed, ignited, and again submitted to the above process on a small scale.

When everything soluble has dissolved, the liquid is filtered through a 9-cm. paper containing a little filter-pulp in the apex. The residue is collected, washed with warm water, ignited in a tared platinum crucible, and treated as under (3), *below*.

(2) Since stannic oxide is slightly attacked by fused bisulphate, the unfiltered hot tartaric acid solution of bisulphate melts obtained from materials containing tin is treated with hydrogen sulphide until cold, the dissolved tin being precipitated as sulphide, which is filtered off with the undissolved silica and tin oxide, and washed with slightly acidulated (sulphuric acid) water containing hydrogen sulphide. After ignition and weighing in a tared platinum crucible the mixture is treated as under (3), *below*.

(3) *Silica preponderates.* The weighed oxide mixture, or the insoluble product from (1) or (2), *above*, is treated in the usual manner with hydrofluoric and sulphuric acids. The fixed residue is strongly ignited and weighed, silica being found by difference. The small residue (if any) is fused with bisulphate, the melt dissolved in a few ml. of tartaric acid solution, and the solution transferred to a beaker and saturated with hydrogen sulphide. Any precipitate is collected and washed as before (2), ignited, and weighed as $SnO_2$. The filtrate containing the earth acids is treated as under § IV, *b*, 2, or added to the main filtrate obtained under (1) or (2). (Further treatment: see *b*, *below*.)

(4) *Stannic oxide preponderates.* The mineral, or the oxide mixture, is heated to redness in a current of hydrogen in a porcelain boat. After cooling under hydrogen, the contents of the boat are transferred to a beaker and digested with hot 1 : 1 hydrochloric acid, which removes the bulk of the tin; the residue is collected, ignited, and treated as under (1) or (3), *above*, as the case may be.

(*b*) *From Metals of the Hydrogen-sulphide Group.*[1]—The tartaric acid filtrate obtained as under *a*, 1, *above*, is saturated with hydrogen sulphide. If tin is present, the bulk of this metal has been eliminated as insoluble stannic oxide, together with silica, by filtration (*a*, 2), the small balance of dissolved tin being precipitated with the other metals of the hydrogen-sulphide group. The sulphide precipitate is collected and washed with hydrogen-sulphide water acidulated with sulphuric acid. (Treatment of filtrate: see *c*, 1 or 2, *below*.)

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[1] E. F. Waterhouse and W. R. Schoeller, *Analyst*, 1932, 57, 284.

The sulphide precipitate, if bulky, may contain a little earth acid: the filter and precipitate are, therefore, returned to the beaker and gently heated with 8 ml. of strong sulphuric acid, while a mixture of equal volumes of strong nitric and sulphuric acids is added drop by drop until all the organic matter is destroyed. The nitric acid is expelled by heating until white fumes are evolved, and the cold mass is treated with 20 ml. of water and 2 to 3 g. of tartaric acid. The solution is warmed till clear, treated with excess of 1 : 1 ammonia, and slowly poured into hot yellow ammonium sulphide solution. The beaker is left on a hot-plate until the precipitate has settled. This is collected, washed with water containing ammonium sulphide, and analysed for copper, bismuth, etc. by known methods.

The filtrate from the copper subgroup is acidified with acetic acid and digested on a hot-plate until the precipitate has coagulated. This is collected, washed, and analysed for antimony and subordinate amounts of tin and copper (the latter metal is slightly soluble in polysulphide solution).

The filtrate from the antimony subgroup contains any small quantities of earth acid occluded in the original sulphide precipitate. This is recovered by tannin precipitation (§ IV, *b*, 2).

(*c*) *From Metals of the Ammonium-sulphide Group.*—This operation can be carried out either in one or two steps: the combination method (tartaric hydrolysis followed by ammonium sulphide precipitation) is adopted where substantial amounts of earth acid and metals are present, or in the case of earth-acid minerals containing a subordinate amount of tungstic oxide, which is coprecipitated with the earth acids.[1] The second step, ammonium sulphide precipitation, supplements tartaric hydrolysis, or is directly applied to solutions containing subordinate amounts of earth acid.

(1) *Tartaric hydrolysis.*[2] The tartrate solution (150 to 250 ml.), containing hydrogen sulphide and the iron in the ferrous state (*e.g.* the filtrate from the sulphide precipitate obtained under *b*), is heated to boiling, stirred, treated with 25 to 35 ml. of strong hydrochloric acid, and gently boiled for about 3 minutes. The flocculent white precipitate, containing the bulk of the niobic, tantalic, and tungstic acids (about 0·003 to 0·01 g. escapes precipitation), is mixed with filter-pulp, collected, and washed with 2 per cent. hydrochloric acid or ammonium chloride solution. If bulky, it is returned to the beaker with the wash-liquor, thoroughly churned up with 100 ml. of liquid, and once more gathered on the same paper. The beaker is thoroughly cleaned with a rubber-tipped glass rod and filter-pulp. The precipitate is ignited wet in a tared silica or porcelain crucible; the filtrate, containing metals of the ammonium-sulphide group and the minor earth-acid fraction, is treated as under (2), *below*.

(2) *Ammonium-sulphide precipitation.* This procedure is the same as that

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[1] W. R. Schoeller and E. F. Waterhouse, *Analyst*, 1936, **61**, 449; W. R. Schoeller and C. Jahn, *ibid.*, 1934, **59**, 465.

[2] W. R. Schoeller and E. C. Deering, *ibid.*, 1927, **52**, 633.

for the separation of other earths from iron, etc. (**XIII,** § III, *c*). The acid solution is saturated with hydrogen sulphide for the reduction of ferric iron, treated with ammonium chloride, excess of ammonia, and again with hydrogen sulphide, and set aside overnight to allow the precipitate to flocculate and settle clear. The earth acids are determined in the filtrate as under § IV, *b*, 2.

To ensure quantitative precipitation of *manganese* as sulphide in this procedure it is necessary to work in very concentrated solution[1]: the filtrate from the hydrolysis precipitate (1, *above*) is evaporated to a small volume, transferred to a squat 250-ml. beaker, and again evaporated until a syrupy liquor is left; this is diluted to about 25 ml. with hot water, treated with hydrogen sulphide until the iron is reduced, then with ammonia in excess and more hydrogen sulphide, and set aside overnight. The manganous sulphide is always obtained as the dense, pale green modification.

(*d*) *From Aluminium, Chromium, Manganese: Cupferron Precipitation.*[2]—The earth acids can be recovered from tartaric, oxalic, or oxalo-tartaric solution by precipitation with cupferron in the same manner as titanium, zirconium, etc. (**XIII,** § III, *e*). The recoveries have a tendency to be low by a mg. or less, as has been proved by application of the micro-method given in § IV, *b*, 3.

(*e*) *From Zirconium.*—(1) *The earth acids preponderate.*[3] The mixed oxides are fused with 3 to 6 g. of potassium carbonate in a platinum crucible over a blast-burner, and the cold melt is extracted with hot 2 per cent. potassium hydroxide solution. The extract is filtered through close-textured paper containing a pad of filter-pulp pressed into the apex, care being taken to obtain a perfectly clear filtrate; if necessary, the solution is once more passed through the same filter. The residue is washed with 1 per cent. potassium carbonate solution. The filtrate contains the bulk of the earth acids (see § IV, *a*); the residue, the whole of the zirconia contaminated with a few mg. of earth (chiefly tantalic) acid: it is treated as under (2), *below*.

(2) *Zirconia preponderates.* If a potassium-carbonate fusion (1, *above*) has been carried out, the insoluble residue from the extraction of the melt is returned to the beaker, the filter is pulped, and hydrochloric acid added followed by ammonia, both in slight excess. Precipitate and pulp are collected, washed a few times with ammonium chloride solution, and ignited in a silica crucible. The above operation removes adsorbed potash, which would attack the crucible. The ignited oxides are treated as under (*f*), *below*.

(*f*) *From Elements of Tannin Group B.*[4]—The mixed oxides are fused with bisulphate, and the melt is dissolved in ammonium oxalate solution; the solution is treated as under **XIII,** § III, *d*. The resultant precipitate contains the earth acids, and titania if present; these are separated as under (*h*), *below*. The filtrate from the tannin precipitate contains zirconia, alumina, thoria, uranic oxide, beryllia, etc.

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[1] W. R. Schoeller and H. W. Webb, *Analyst*, 1934, **59**, 667.
[2] H. Pied, *Compt. rend.*, 1924, **179**, 897.
[3] W. R. Schoeller and E. F. Waterhouse, *Analyst*, 1928, **53**, 515.
[4] W. R. Schoeller and A. R. Powell, *ibid.*, 1932, **57**, 550.

(*g*) *From Tungstate.*—(1) *The earth acids preponderate: magnesia method.*[1] The mixed oxides (0·2 to 0·5 g.) are fused with 4 to 6 g. of potassium carbonate in a platinum crucible over a blast-burner till the melt is clear. After cooling it is dissolved in hot water (100 to 200 ml.); the solution is heated almost to boiling, stirred, and precipitated drop by drop with 25 to 40 ml. of a freshly prepared slightly ammoniacal solution of 4 g. of crystallized magnesium sulphate and 8 g. of ammonium chloride in 100 ml. of water. After settling for 10 to 15 minutes on the water-bath the white flocculent precipitate of magnesium niobate and tantalate is collected, and well washed with 2 per cent. ammonium chloride solution.

If the quantity of tungstic oxide present exceeds 0·02 g., it is advisable to repeat the separation. The magnesia precipitate is rinsed back and digested with a little dilute hydrochloric acid. The suspension is boiled and treated with 5 g. each of ammonium chloride and acetate and a solution of 0·5 to 1 g. of tannin. The precipitate is mixed with filter-pulp, collected, washed with 2 per cent. ammonium nitrate solution containing a little tannin, and ignited in the platinum crucible. The ignited oxides are again treated by fusion with potassium carbonate and precipitation with magnesia mixture, the second magnesia precipitate being converted into oxides by the procedure just described, and weighed as $(Ta,Nb)_2O_5$ (major fraction).

The filtrate or combined filtrate from the magnesia precipitation contains the whole of the tungstic acid and usually a little niobic acid, unless tantalic acid largely predominates in the oxide mixture. It is treated with 10 to 20 g. of ammonium chloride, and the tungstic and niobic oxides recovered by the tannin-cinchonine method (**XXI,** § IV, *c*). If the tannin precipitate prior to the addition of cinchonine solution is coffee-brown, and yellow after ignition, its niobium content (if any) is very small; if, on the other hand, it is reddish-brown or even reddish (with low tungsten contents), and pale yellow to white after ignition, it is certain to contain niobium.

In any case the purity of the ignited weighed tannin-cinchonine precipitate should be tested by the sodium hydroxide method (2, *below*).

The magnesia method separates tungstic oxide, not only from the earth acids, but from titania, zirconia, and complex mixtures of all the earths.

(2) *Tungstic oxide preponderates: sodium hydroxide method.*[2] This method is applicable to the determination of small quantities of pentoxides in tungstic oxide, as well as to the complete separation of the last of the niobium from the tungstic oxide obtained by the magnesia method (1, *above*).

The mixed oxides are fused with sodium hydroxide in a nickel crucible. In the case of substantially pure tungstic oxide, 1 g. is fused with 2 g. of the alkali; smaller precipitates obtained by the magnesia method are fused with 0·2 to 0·5 g. The heat is raised to redness for a short time, when a clear melt results. After cooling, it is dissolved in the crucible in a minimum of warm, half-saturated sodium chloride solution. The solution is transferred to a small beaker and set aside for two or more hours in the cold, to allow the pulverulent precipitate of sodium niobate (tantalate) to settle. This is collected on a small, tight pad of filter-pulp in a small funnel, care being taken to ensure a perfectly clear filtrate; refiltration may be necessary. The precipitate is washed with a minimum of half-saturated sodium chloride solution in portions of 2 to 3 ml., returned to the beaker with the pad, and treated with dilute hydrochloric acid followed by a slight excess of dilute ammonia. Precipitate and pulp are collected on a small filter, washed with 2 per cent. ammonium chloride solution, ignited, and weighed as $(Nb,Ta)_2O_5$. (In the magnesia method, this constitutes the minor earth-acid fraction.)

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[1] A. R. Powell, W. R. Schoeller, and C. Jahn, *Analyst*, 1935, **60**, 509.

[2] W. R. Schoeller and C. Jahn, *ibid.*, 1927, **52**, 513.

The alkaline filtrate from the sodium-salt precipitate, containing sodium tungstate, is treated with ammonium chloride, etc. for the recovery of the tungstic oxide, as described under (1). The ignited $WO_3$, which is yellow and free from niobium, is weighed. In the case of pentoxide determinations in 1-g. portions of tungstic oxide, the latter is taken by difference.

(*h*) *From Titania.*—(1) *Titania preponderates: pyrosulphate-tannin method.*[1] The mixed oxides (not more than 0·25 g.) are fused with 1 to 4 g. of potassium bisulphate in a silica crucible, and the melt spread in a thin layer round the sides of the crucible. The reagent for the separation is a freshly prepared 1 per cent. solution of tannin in 5 per cent. sulphuric acid. The crucible is filled with the reagent and warmed, the melt detached with a glass rod and transferred to a 250-ml. beaker, and the crucible rinsed with further portions of reagent (50 to 100 ml. in all) with the aid of a rubber-tipped rod. The liquid is heated on a water-bath for half an hour with occasional agitation, and set aside in the cold for some hours or overnight. The coloured precipitate, consisting of the tannin complexes of the earth acids, is collected, washed with 5 per cent. sulphuric acid, ignited, and weighed as $(Nb,Ta)_2O_5$.

If the absolute amount of titania is high (more than 0·1 g.), the weighed pentoxides should be fused with bisulphate, and the process repeated.

The final pentoxide precipitate is tested colorimetrically for titania (2, *below*), the amount found being subtracted from the weight of the pentoxides. The net result shows a slight negative error, especially if niobic oxide preponderates over tantalic oxide.

The pyrosulphate-tannin method is applicable also to the separation of zirconia, or a mixture of zirconia and titania, from small quantities of earth acid. In fact, it can be used as an earth-acid test in other earths giving soluble sulphates.

(2) *Colorimetric determination of titania in the pentoxides.* Small quantities of titania in the pentoxides are determined colorimetrically as pertitanic acid without any separation. The procedure is as follows:

The mixed oxides are fused with 2 g. of potassium bisulphate in a silica crucible, and the melt is dissolved by warming in a solution of 3 g. of ammonium oxalate. The solution is transferred to a 200-ml. graduated flask with 50 ml. of 10 per cent. sulphuric acid to which a little sodium peroxide has been added, cooled, adjusted to 200 ml., and an aliquot portion matched in a Nessler tube against a standard prepared with the same quantities of bisulphate, ammonium oxalate, and sulphuric acid containing peroxide. It is convenient to use a stock solution containing 30 g. each of potassium bisulphate and ammonium oxalate per litre. (Standard titanium solution: see **XIII**, § VI.)

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[1] W. R. Schoeller, *Analyst*, 1929, **54**, 455; W. R. Schoeller and C. Jahn, *ibid.*, 1932, **57**, 74.

(3) *The earth acids preponderate: oxalate-salicylate method.*[1] This is the standard process for the separation of titania from the earth acids, which, whilst applicable to mixtures of titania and pentoxides in any proportions, is used for the removal of titania from substantial quantities of earth acids prior to the separation of tantalum from niobium by the tannin process (*i, below*). The process depends upon the action of sodium salicylate upon a solution of the oxalo-complexes of the three elements, soluble orange-coloured titanylsalicylic acid being formed, while the oxalo-earth acids remain unaffected. Subsequent addition of calcium chloride removes the whole of the oxalate from the solution, and the earth acids are precipitated (together with calcium oxalate) as insoluble salicylic complexes: the tantalum precipitate is white, the niobium precipitate yellow.

The mixed oxides (0·25 g. or less) are fused with 3 g. of potassium bisulphate, and the melt is dissolved in a hot solution of 2 to 2·5 g. of ammonium oxalate in an 800-ml. beaker. The solution (150 to 250 ml.) is heated to boiling, treated with 5 g. of sodium salicylate B.P. (a yellow to bright orange colour develops according to the amount of titania present), and precipitated slowly while stirring with 40 to 50 ml. of 10 per cent. calcium chloride solution. The beaker is removed to the hot-plate, and stirring is continued until the precipitate settles clear (15 minutes or less), the supernatant liquid being tested for complete precipitation with a little calcium chloride. The solution should not be allowed to cool.

The precipitate is collected under slight suction on an 11-cm. filter, and washed with hot 2 per cent. sodium salicylate solution until the washings are colourless. (Precipitate: $P^1$; filtrate: $F^1$.)

$P^1$: *major earth-acid fraction.* The filter is spread against the side of the 800-ml. beaker and rinsed down with hot water, 40 to 50 ml. of 1 : 1 hydrochloric acid, and again with water, the paper incinerated, and the ash added. The suspension is heated (the precipitate dissolving), and the solution is stirred and treated with saturated potassium permanganate solution until it remains brownish-black, indicating complete elimination of the oxalic acid. If frothing occurs during the oxidation, the sides of the beaker should be washed down with hot water. The discoloured boiling liquid (200 ml.) is heated with a strong solution of 1 to 2 g. of tannin, which at once reduces the higher oxides of manganese and converts the earth acids into coloured adsorption complexes. Precipitation is completed by addition of 20 g. each of ammonium chloride and acetate, and of filter-pulp. The precipitate is collected under slight suction on an 11-cm. filter, thoroughly washed with 2 per cent. ammonium chloride solution, transferred to a silica crucible, and reserved ($P^{1a}$).

$F^1$. The coloured filtrate is transferred to a 600-ml. beaker, treated with 10 g. each of ammonium acetate and chloride, boiled, and precipitated with 1·5 to 3 g. of tannin in fresh, strong solution. The red precipitate is mixed with pulp, collected under suction if bulky, washed with 2 per cent. ammonium chloride solution, and ignited wet in a silica crucible. It consists of the major titania fraction containing a few mg. of pentoxides, which are recovered as $\pi^1$.

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[1] W. R. Schoeller and C. Jahn, *Analyst*, 1932, **57**, 75.

*Minor earth-acid fraction.* The ignited titania precipitate from $F^1$ is fused with bisulphate, and the melt is treated by the pyrosulphate-tannin method (1, *above*). This yields a filtrate, $F^{1a}$, containing the purified titania fraction, and a small tannin precipitate, $\pi^1$, consisting of the minor earth-acid fraction: this is added to the silica crucible containing $P^{1a}$, and the combined precipitates are ignited, and weighed as $(Ta,Nb)_2O_5$.

$F^{1a}$: *titania fraction.* This is recovered from the filtrate $F^{1a}$ by partial neutralization with ammonia, addition of ammonium acetate and chloride, and boiling with more tannin, etc. as for $F^1$. The precipitate is ignited to $TiO_2$.

*Retreatment of earth-acid fraction.* The titania obtained in the preceding paragraph is a final product, but the earth-acid fraction $(P^{1a}+\pi^1)$ retains a little titania. This can, of course, be determined colorimetrically (2, *above*), but if it exceeds 1 to 2 mg. it may interfere in the tannin separation of tantalum for niobium, as explained under (*i*). The lower the tantalum content of the mixed pentoxides, the stronger the interference of titania in the tantalum-niobium separation. Therefore, if the absolute amount of titania in the mixed oxides under treatment is higher than 0·01 g., it will usually be necessary to repeat the oxalate-salicylate procedure on $(P^{1a}+\pi^1)$.

The retreatment is carried out in precisely the same manner as the first, yielding $P^{2a}$ (major) and $\pi^2$ (minor) earth-acid fractions, and a very small titania fraction, which is added to that obtained in the first treatment.

The sum of the oxides obtained in this method is normally 1 to 3 mg. less than the mixed oxides taken; this negative error, due to a little earth acid escaping recovery, is added to the pentoxide result, and subsequently apportioned between the tantalic and niobic oxides after tannin separation (*i, below*).

(*i*) *Tantalum from Niobium: Tannin Method.*[1]—This method is based on the fact that tantalic oxide is more readily precipitated by tannin from slightly acid oxalate solution than any other earth in general and niobic oxide in particular: it comes first in the serial order of precipitability, titania coming next, and niobic oxide third.

A clean-cut separation cannot be accomplished in a single precipitation, since tantalum cannot be quantitatively precipitated without appreciable coprecipitation of niobium; hence a process of fractional precipitation has to be adopted. This can be controlled because the colour of the precipitated tantalum-tannin complex is a reliable indicator of its purity. The pure tantalum complex is light yellow; the niobium complex, which is bright vermilion-red, possesses strong colouring power, hence a small admixture of niobium imparts an orange-yellow to orange colour to the tantalum precipitate.

It will be readily understood that titania should be either absent or very subordinate in amount, since it is partly coprecipitated with tantalum before any niobium is precipitated, and its red tannin complex produces a buff to brownish discoloration of the tantalum precipitate, thus masking the colour changes on which the process wholly depends. If, however, the titania present is well below 2 per cent. of the tantalic oxide, the interference is not sufficiently marked to vitiate the results (though the tantalum precipitate will always be dark yellow instead of light yellow); in such cases the quantity of titania in the separated oxides is determined colorimetrically. About 75 per cent. of the titania passes into the tantalum fraction.

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[1] A. R. Powell and W. R. Schoeller, *Analyst*, 1925, **50**, 485; W. R. Schoeller, *ibid.*, 1932, **57**, 750.

The fractionation process furnishes three products: (1) a niobium-free tantalum fraction (yellow precipitates), (2) a mixed or intermediate fraction (orange to red precipitates), and (3) a tantalum-free niobium filtrate. The second fraction is retreated, giving another three fractions, the intermediate one of which is again fractionated. The pure tantalum fractions are ignited together, and the niobium filtrates combined.

If niobium distinctly preponderates, no yellow head-fraction will be obtained in the first fractionation. After one or two repetitions, the intermediate fraction will become very small; the total error is confined to that incurred in the precipitation of the final small tantalum fraction, which should be produced as a slightly niobiferous, pale orange precipitate, for the purpose of counteracting incomplete recovery of the tantalum.

The precipitates are designated as follows:

first fractionation: $P^1$, $P^{1a}$, $P^{1b}$, $P^{1c}$;
second fractionation (retreatment of first intermediate fraction): $P^2$, $P^{2a}$, $P^{2b}$;
third fractionation (retreatment of second intermediate fraction): $P^3$, $P^{3a}$.

The tannin precipitates are mixed with a little filter-pulp, and washed with hot 2 per cent. ammonium chloride solution; if bulky, they are collected under slight suction. Purification: see (2) and (3), *below*.

(1) *The fractionation.* The mixed pentoxides, containing not more than 0·2 g. $Ta_2O_5$, are fused with potassium bisulphate in a silica crucible, and the melt is dissolved in a hot solution of 3 to 4 g. of ammonium oxalate. The hot solution is filtered into a 600-ml. beaker, any small siliceous residue being ignited and its weight deducted; retreatment is sometimes advisable.

*First fractionation.* The filtrate (or combined filtrate, 200 to 250 ml.) is boiled and treated gradually with 10 to 15 ml. of a freshly prepared 2 per cent. solution of tannin; this will cause either a yellow or an orange to red coloration. The two cases will be dealt with separately:

*Case A: yellow coloration: tantalum preponderates.* If the tantalum content is very high, the boiling yellow solution soon turns cloudy and a yellow precipitate gradually forms. More tannin is cautiously added, and the effect noted: a transient orange tint disappearing upon agitation denotes incipient formation and decomposition of the niobium complex. The addition of tannin is interrupted before the orange tint becomes permanent. The maximum addition of tannin reagent is 40 to 50 ml. (for 0·2 g. $Ta_2O_5$, with less than 0·05 g. $Nb_2O_5$). Complete flocculation is brought about by addition of 25 ml. of saturated ammonium chloride solution and a few minutes' gentle boiling.

*First fraction*: $P^1$. The yellow precipitate, $P^1$, is collected, washed, and ignited in a tared porcelain crucible reserved for the tantalum fraction. While the precipitate is being washed the filtrate is boiled down, the volume of the solution being kept approximately constant during each fractionation.

*Second fraction*: $P^{1a}$. The concentrated filtrate and washings from $P^1$ are boiled, treated with 5 to 10 ml. of tannin reagent, and slowly titrated with N. ammonia during constant agitation. This produces at the point of incidence an orange cloudiness, which flocculates on stirring to a yellow ($\alpha$) or an orange ($\beta$) precipitate.

($\alpha$) If the precipitate is yellow (high tantalum content), the addition of ammonia is interrupted before the colour of the precipitate changes to orange; the yellow precipitate, $P^{1a}$, is collected, washed, added to the crucible containing $P^1$, and ignited.

($\beta$) If the precipitate is orange, the dropwise addition of ammonia is continued until the colour of the precipitate appears to change to orange-red. The precipitate, $P^{1a}$, is collected, washed, and ignited in a silica crucible.

*Third fraction*, $P^{1b}$. The treatment of the concentrated filtrate and washings from $P^{1a}$ depends upon the alternatives just considered:

($\alpha$) Yellow $P^{1a}$. The boiling solution is stirred, treated with 5 ml. of tannin reagent, and slowly titrated with N. ammonia. An orange precipitate, $P^{1b}$, is produced, the directions given under ($\beta$), *above*, being followed. The washed precipitate is ignited in a silica crucible.

($\beta$) Orange $P^{1a}$. The boiling solution is stirred, treated with 5 ml. of tannin reagent, and titrated with N. ammonia. The precipitate, $P^{1b}$, should now be red, which proves that the whole of the tantalum has been precipitated. The addition of ammonia is interrupted when about 0·01 g. (or less) of pentoxide has been precipitated. The precipitate is left on a hot-plate until it has gathered into red flocks, when it is collected, washed, and ignited together with $P^{1a}$.

*Fourth fraction*: $P^{1c}$. This need only be produced in the case of $P^{1b}$, $\alpha$: the concentrated filtrate from $P^{1b}$ is treated with 5 ml. of tannin reagent, boiled, stirred, and slowly titrated with N. ammonia, the directions given under $P^{1b}$, $\beta$, *above*, being followed. The washed precipitate is ignited together with $P^{1b}$.

An experienced operator can carry out the first fractionation in about 4 hours. To recapitulate, either 3 or 4 fractions are obtained in the above procedure:

| Fractions. | High $Ta_2O_5$. | Medium High $Ta_2O_5$. |
|---|---|---|
| $P^1$ | Yellow Ta fractions | Yellow: Ta fraction |
| $P^{1a}$ | Yellow combined | Orange Mixed fractions |
| $P^{1b}$ | Orange Mixed fractions | Red combined |
| $P^{1c}$ | Red combined | .. |

The combined mixed fractions are retreated (see "Second fractionation," *below*).

*Case B: orange to red coloration: niobium preponderates.* Only two fractions are produced, corresponding to $P^{1b}$ and $P^{1c}$, Case A, *a*.

*First fraction*: $P^1$. The addition of tannin is restricted to 10 to 15 ml. The boiling solution is treated with 25 ml. of saturated ammonium chloride solution, stirred, and titrated with N. ammonia until the colour of $P^1$ is decidedly red (*cf.* "second fraction," *β*, *above*). The precipitate, $P^1$, is ignited in a silica crucible.

*Second fraction*: $P^{1a}$. The filtrate and washings from $P^1$ are treated with 5 ml. of tannin reagent, and titrated with N. ammonia until about 0·01 g. of pentoxide has been precipitated (*cf.* "third fraction," *β*, *above*). The precipitate, $P^{1a}$, which is left to flocculate on a hot-plate, should be bright red; it is collected, washed, and ignited together with $P^1$.

The ignited fractions are retreated (see "Second fractionation," *below*).

*Second fractionation.* The combined intermediate fractions ($P^{1b}+P^{1c}$) or ($P^{1a}+P^{1b}$), Case A, or the combined mixed fractions ($P^1+P^{1a}$), Case B, are ignited in a silica crucible, fused with bisulphate, and the melt is dissolved in hot ammonium oxalate solution. The resultant solution is fractionated exactly like that of the original mixed oxides, but on a reduced scale. Three fractions are usually produced:

$P^2$, yellow: added to tantalum fraction;
$P^{2a}$, orange } combined and retreated in the third (normally final)
$P^{2b}$, red } fractionation.

If the head-fraction $P^2$, obtained from ($P^1+P^{1a}$) in Case B, is still orange, a very low tantalum content is indicated. In such a case, two fractions are produced:

$P^2$, orange } combined and retreated in third fractionation.
$P^{2a}$, red }

*Final fractionation.* For the proper control of the operations, it is indispensable that each fraction be weighed to the nearest mg. The original weight of the mixed oxides, the volume of reagent added, and the colour and weight of all the fractions are reliable data for the progress of the separation.

The final fractionation is undertaken when the weight of the combined intermediate fraction has been reduced to about 0·01 g. Two fractions are normally produced:

$P^3$, yellow } added to tantalum fraction.
$P^{3a}$, pale orange }

The error incurred by the coprecipitation of niobium in $P^{3a}$, which under expert control does not exceed 0·004 g. in weight, is less than 0·001 g.

(2) *Determination of tantalic oxide.* The weight of the combined precipitates representing the tantalum fraction must be corrected for any adsorbed salts and traces of lime, and for titania and silica (filter-ash). The oxide is leached with 2 per cent. hydrochloric acid, collected, ignited strongly, weighed, and fused with bisulphate. The melt is dissolved in ammonium oxalate solution with the addition of dilute sulphuric acid and a little sodium peroxide. The small residue is collected, washed, ignited, and weighed.

The titania in the filtrate is determined colorimetrically (*h*, 2, *above*). The weights of the siliceous residue and titania, subtracted from the weight of the leached precipitate, give the net weight of $Ta_2O_5$. If the titania has been previously separated by the oxalate-salicylate method, the small loss incurred in that operation is distributed between the tantalic and niobic oxides in the proportion of the ratio found.

(3) *Determination of niobic oxide.* As the niobic oxide is a final product, it is usually sufficient to take it by difference. Should it be considered necessary to make a direct determination, the combined filtrates obtained in the fractionation are boiled and precipitated with more tannin and slight excess of ammonia. The precipitate is collected under slight suction, washed with 2 per cent. ammonium chloride solution, ignited, and weighed. As in the case of the tantalum fraction, the weight of the ignited precipitate must be corrected for adsorbed salts, lime, silica, titania, and probably traces of ferric oxide (*c*, 2, *above*).

§ **IV. Gravimetric Determination.**—In accurate analytical work, niobium and tantalum are always determined gravimetrically in the form of their pentoxides. These are obtained by ignition of the hydrated earth acids, their tannin complexes, or the cupferron precipitates.

(*a*) *Precipitation of the earth acids* as such is effected either by tartaric hydrolysis (§ III, *c*, 1) or by decomposition of their potassium or sodium salts with a mineral acid.

Potassium niobate and tantalate are obtained by fusion of the pentoxides (or earth-acid minerals) with potassium hydroxide or carbonate. For the recovery of the pentoxides, the diluted solution is heated to boiling and acidified with hydrochloric or nitric acid. By addition of a slight excess of ammonia to the acidified solution, the earth acids are obtained as a coarsely flocculent white precipitate which settles much more readily than that obtained by acidification, and gives a perfectly clear filtrate.

Sodium niobate and tantalate are obtained as finely crystalline or pulverulent precipitates when the fairly concentrated solution of the potassium salts is saturated with solid sodium chloride; the precipitates are filtered off and washed with half-saturated sodium chloride solution.[1] The washed precipitate is returned to the beaker with the filter, the paper is pulped, the diluted suspension boiled, and treated with a slight excess of acid followed by ammonia as in the case of the potassium salts.

However obtained, the precipitated earth acids are mixed with filter-pulp, collected, returned to the beaker with hot 2 per cent. ammonium chloride solution, churned up and returned to the filter, and the beaker is cleaned with filter-pulp. The washed precipitate is ignited in a porcelain or silica crucible, finally over a blast-burner for about 15 minutes. It readily attains constant weight.

(*b*) *Precipitation of the tannin complexes* is carried out either in oxalate or in tartrate solution.

(1) *The precipitation from oxalate solution* has been described under

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[1] Any alkali tungstate present passes wholly into the filtrate. The procedure provides a third method for the separation of tungsten from tantalum and niobium (*cf.* § III, *g*, 1).

**XIII,** § III, *d*, the conditions for the quantitative precipitation of the earth acids being the same as for titania. The same rules apply for the ignition and purification of the tannin precipitates. For the gravimetric determination of the separated pentoxides, see § III, *i*, *above*.

(2) *The precipitation from tartrate solution* is conducted as follows: If the tartrate solution contains ammonium sulphide, it is acidified with hydrochloric acid and boiled till free from hydrogen sulphide. After slight cooling, it is rendered faintly ammoniacal, and the excess of ammonia expelled by boiling; 10 to 20 g. of ammonium chloride and 10 g. of ammonium acetate are then added, followed by a concentrated solution containing tannin equal to 10 to 15 times the weight of the pentoxides (at least 0·5 g.). The liquid is boiled for a few minutes, and the tannin precipitate mixed with pulp, collected, washed, ignited, and purified as *above*.

(3) *Micro-method.* The process described *below* is applied for the determination of the earth acids on a mg. scale in large volumes of solution or in substantial quantities of siliceous residues as obtained, for example, by the usual procedures of silicate analysis.

Solutions containing ammonium chloride, organic acids, etc. are evaporated with excess of nitric and sulphuric acids to complete destruction of the ammonium salts and organic matter. Solutions containing ammonium nitrate or sulphate are evaporated with *aqua regia*, and once more with nitric and sulphuric acids. The residual liquid containing sulphuric acid is transferred to a silica dish, in which the acid is boiled off. The residue is dissolved in hot water, the solution made ammoniacal, and the precipitate collected, washed, and ignited in a platinum crucible.

The ignited precipitate, or the original siliceous residue to be tested, is heated with hydrofluoric and sulphuric acids as usual, the residue fused with a little potassium bisulphate, and the melt dissolved in a few ml. of ammonium oxalate solution. The resultant solution is treated in a 50-ml. beaker with an equal volume of strong ammonium chloride solution and about 0·02 to 0·05 g. of tannin, stirred, and titrated while boiling with 0·02N. ammonia added through the fine jet of a small burette. When the solution is nearly neutral, a coloured tannin precipitate of the earth acids (titania) will be obtained. If neutralization proceeds too far, the tannin precipitate may turn dirty white (aluminium) or mauve (iron); addition of a few drops of 0·1N. hydrochloric acid will remove the discoloration. The deep yellow, orange, or red precipitate is collected on a 5-cm. filter, washed with ammonium chloride solution, ignited, and weighed as $TiO_2 + (Nb,Ta)_2O_5$.

The weighed precipitate is fused with a speck of bisulphate, the melt dissolved in ammonium oxalate solution, and any titania present determined colorimetrically (§ III, *h*, 2). The solution is evaporated to dryness in a silica dish and the residue fused with a little more bisulphate. If titania has been found to be present, the pyrosulphate-tannin method (§ III, *h*, 1) is applied on a small scale; the coloured residue of earth-acid complexes is collected, washed, ignited, weighed as a check, and fused with bisulphate. This melt, or the previous one if titanium was absent, is dissolved in ammonium oxalate solution, and the tannin separation method (§ III, *i*) applied on a reduced scale. On account of the bulkiness and characteristic colour of the precipitates, the tannin method is the only suitable process for micro- or semi-micro-work.

(*c*) *Cupferron Precipitation.*—Earth-acid precipitates obtained by the cupferron method are treated in exactly the same manner as titania precipitates as regards incorporation of filter-pulp, suction filtration, ignition, etc. (**XIII**, § III, *e*).

§ **V. Volumetric Determination.**—The volumetric methods for niobium and tantalum are not sufficiently reliable for accurate work. They comprise (*a*) oxidimetric processes for niobium, and (*b*) an acidimetric process for both elements.

(*a*) *Oxidimetric Niobium Determination.*—Many attempts have been made to solve the problem of the separate determination of niobium and tantalum by volumetric methods based on the reducibility of niobium pentoxide with zinc to a lower oxide and re-oxidation of the latter by permanganate. As tantalic oxide is not reducible in solution, it was thought that the difficult separation of the two elements by Marignac's fluoride method [1] could be avoided by the use of the oxidimetric method. The two processes usually described in the literature are F. J. Metzger and C. E. Taylor's [2] (involving the use of succinic acid to prevent hydrolysis) and A. G. Levy's modification [3] of Osborne's fluoride method.[4]

We consider it unnecessary to give a description of these processes, for they suffer from a common defect, incomplete reduction, which gives rise to variable, non-reproducible factors.[5] This is due to partial hydrolysis of the niobic salt, resulting in a colloidal phase which escapes reduction.[6]

Another fatal objection to the oxidimetric method for niobium is that materials containing niobium and tantalum are seldom free from titania, which also is reduced to a lower oxide, and increases the uncertainty as to the degree of reduction of the niobium.

Now that reliable gravimetric methods for the separation of niobium, tantalum, and titanium are available, the use of the unsatisfactory volumetric procedures is no longer justified.

(*b*) *Approximate Simultaneous Acidimetric Determination of Niobium and Tantalum.*—This rapid process is based on the conversion of the earth acids into their insoluble sodium salts, obtained as described under § IV, *a*, *above*. The composition of the precipitates is expressed by the formulæ: $4Na_2O.3Ta_2O_5$ and $7Na_2O.6Nb_2O_5$ (4 : 3 sodium tantalate and 7 : 6 sodium niobate). The suspension of the precipitates (washed free from alkali carbonate by half-saturated sodium chloride solution) can be titrated with 0·1N. hydrochloric acid in presence of methyl-orange, but the end-point is not very sharp. As in all indirect titration methods, the mixed oxides should contain substantial proportions of each constituent. The error is of the order of 2 per cent. when 0·5 g. of mixed oxides is used. Full details of the process are given in W. R. Schoeller's monograph.[7]

§ **VI. Detection in Minerals.**—In many text-books on qualitative analysis, niobium and tantalum have been, and still continue to be, erroneously represented as members of the third qualitative group, the earth acids being included in the general group-precipitate produced by ammonia in an acid solution. Actually the two elements form only acidic oxides which are incapable of forming soluble simple salts with the common acids, in which respect they may be grouped together with tungsten and silicon. Ammonia precipitates the earth acids from fluoride or oxalate solution, but neither hydrofluoric nor oxalic acid is employed in the old qualitative scheme, which was intended for chloride, nitrate, or sulphate solutions containing a limited number of common metallic elements.

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[1] *Ann. Chim. Phys.* (4), 1866, **8**, 5, 49.

[2] *J. Soc. Chem. Ind.*, 1909, **28**, 818.

[3] *Analyst*, 1915, **40**, 204.

[4] *Amer. J. Sci.* (3), 1885, **30**, 328.

[5] W. R. Schoeller and E. F. Waterhouse, *Analyst*, 1924, **49**, 215.

[6] W. D. Treadwell, *Helv. Chim. Acta*, 1922, **5**, 806.

[7] *Op. cit.*, pp. 32–36.

(*a*) *Joint Detection of Niobium and Tantalum.*—(1) *Tartaric hydrolysis.* The mineral is fused with bisulphate, and the melt is dissolved in hot 20 per cent. tartaric acid solution (§ III, *a*, 1). The filtered solution is boiled with one-quarter of its volume of strong hydrochloric acid. A white flocculent precipitate, separating either at once or after a few minutes' boiling, is a certain indication of the presence of earth acid. The only other element reacting under the same conditions is tungsten, which gives a yellow precipitate.

If it is desired to identify tantalum and niobium separately, the precipitate produced as *above* should be filtered off and washed with dilute hydrochloric acid (*b*, 1, *below*).

(2) *Tannin test.*[1] This reaction can be carried out with a few mg. of mineral. The fine powder is fused with a little bisulphate, and the melt dissolved in a few ml. of hot saturated ammonium oxalate solution. The liquid is boiled with an equal volume of saturated ammonium chloride solution and 0·02 g. of tannin: a flocculent orange to red precipitate reveals the presence of earth acid, or titania, or both.

Titania should be tested for in a separate portion by the peroxide test (**XIII**, § VII, *a*, 1), and if it is present in the ore, the earth-acid test should be conducted as follows:

The bisulphate melt of the mineral is extracted with a 1 per cent. solution of tannin in 5 per cent. sulphuric acid. A red to orange residue characterizes the earth acids. The residue may be collected on a small filter, washed with dilute sulphuric acid, ignited, and fused with bisulphate; the melt is dissolved in ammonium oxalate solution, and the solution tested with tannin as directed *above*.

(3) *Sodium-chloride precipitation.* The powdered mineral is fused with potassium hydroxide in a nickel, or potassium carbonate in a platinum, crucible. The fused mass is extracted with little water, the extract filtered, and the filtrate saturated with solid sodium chloride. A white crystalline precipitate of sodium niobate and tantalate is obtained (distinction from tungstate).

Antimony is the only other element apt to yield a similar precipitate (sodium antimonate) under the above conditions. The solution of sodium antimonate in tartaric and hydrochloric acids, however, gives a red precipitate on treatment with hydrogen sulphide; while antimonic acid does not give a coloured tannin adsorption-complex when the following test is applied:

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[1] W. R. Schoeller, *Zeitsch. anal. Chem.*, 1934, **96**, 252.

The filtered extract from the potassium hydroxide fusion, acidified with sulphuric acid, gives a white precipitate of earth acids. If tannin solution is added to the suspension, the precipitate turns yellow to orange.

(*b*) *Separate Identification of Niobium and Tantalum.*—There are three specific reactions available for the differentiation of niobium and tantalum: (1) tannin (red niobium precipitate, yellow tantalum precipitate); (2) zinc dust in phosphoric acid solution (dark coloration with niobium, no coloration with tantalum); and (3) potassium fluoride in fluoride solution (no precipitate with niobium, crystalline precipitate with tantalum).

(1) *Tannin.* Of the three, the tannin test is by far the most important, and is to be preferred to the exclusion of others. The success of the test depends upon the absence of appreciable quantities of titania, a very common mineral associate of the earth acids. Titania takes its place between tantalum and niobium in the serial order of precipitability by tannin (§ III, *i*); hence, whilst tantalum is precipitated first, titanium if present is always coprecipitated to a certain extent, and a small admixture of its red tannin complex imparts a brown tint to the otherwise sulphur-yellow tantalum precipitate.

These observations explain the erroneous statement, made in most text-books,[1] to the effect that tantalum gives a yellow-brown or light brown tannin precipitate.

Such is definitely not the case: a tantalum solution that gives a light brown tannin precipitate contains titania. Still, in testing minerals for tantalum, a light brown precipitate is obtained more frequently than a yellow one, on account of the regular association of the two elements and the elaborate manipulation required for the more or less complete elimination of the titania.

For the separate identification of tantalum and niobium by means of tannin, it is best to use the precipitate produced by tartaric hydrolysis (*a*, 1, *above*). The washed precipitate is fused with bisulphate. Before proceeding with the identification of tantalum and niobium, the operator should convince himself that the mixed oxides are reasonably free from titania, since otherwise the characteristic colour of the tantalum precipitate will be masked.

A small portion of the bisulphate melt is accordingly detached and dissolved in ammonium oxalate solution, and the solution tested with hydrogen peroxide; if it remains colourless or turns only pale yellow, the bulk of the bisulphate melt is tested as under ($\alpha$), *below*. If, on the other hand, a pronounced yellow or an orange coloration is obtained, the melt should be treated as under ($\beta$).

($\alpha$) If the melt is almost free from titania, it is dissolved in hot ammonium oxalate solution, and the boiling solution precipitated with 0·1 to 0·2 g. of tannin, a little strong ammonium chloride solution, and a few drops of N. ammonia if necessary to promote flocculation as described in § III, *i*. If the precipitate thus obtained is pale to bright yellow—or a pale yellow-brown, due to a little titania—the presence of tantalum is proved. If, however, the precipitate is orange to red (proving niobium to preponderate), it must be collected, washed, ignited, fused with bisulphate, and the whole process repeated. The second precipitate thus obtained will now be yellow unless the amount of tantalum is very small, in which case the precipitate must be collected and a third precipitation made. The tannin process is the only wet method by which minute amounts of tantalum can be detected (and determined) in presence of a thousandfold excess of niobium. To this end the treatment of the head-fraction must be repeated 5 to 6 times.

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[1] *E.g.* R. J. Meyer and O. Hauser's monograph, *Die Analyse der seltenen Erden und der Erdsäuren*, Stuttgart, 1912, p. 188. The text on that page (lines 11–17) proves that the writer (O. Hauser) was aware of a differential precipitability between tantalum and niobium by tannin in fluoride solution, without, however, apprehending its momentous implication.

Subordinate amounts of niobium are readily detected in the filtrate from the yellow tantalum precipitate by boiling and adding more tannin and 2 to 3 g. of ammonium acetate, a voluminous red precipitate being obtained (it may be orange if the precipitation of the tantalum has been incomplete, and it may be retreated if desired).

($\beta$) If the melt contains an appreciable amount of titania, it should be treated by the pyrosulphate-tannin method (§ III, *h*, 1). The coloured residue from the extraction with the acid tannin solution is collected, washed with 5 per cent. sulphuric acid, ignited, and tested as under ($\alpha$), *above*.

(2) *Zinc dust in phosphoric acid solution.*[1] This test is useful for the detection of small amounts of niobium in the presence of much tantalum. The mineral is fused with potassium carbonate, the filtered aqueous extract of the melt acidified with phosphoric acid and evaporated to a syrup, when the precipitated earth acid will redissolve. The mass is diluted with twice its volume of water; when boiled with 1 g. of zinc dust, the liquid turns black, brown, or yellow, according to the amount of niobium present.

(3) *Potassium fluoride in fluoride solution.*[2] The precipitation of potassium fluorotantalate ($K_2TaF_7$, colourless rhombic needles), at one time the only, though far from perfect, procedure for the separation of tantalum from niobium, is not a sensitive test for tantalum, the precipitate being soluble in 200 parts of cold water or dilute hydrofluoric acid.

§ **VII. Determination in Ores and Alloys.**—(*a*) *In Columbite and Tantalite.*—Within the last two or three years the output of tantalite and columbite has increased steadily, and the analysis of these ores has become a matter of daily routine in certain metallurgical laboratories. As the result of our extensive research as well as commercial experience we can recommenp our "tartaric acid method" given *below* to the exclusion of the older processes, involving either fusion with alkaline fluxes or prolonged boiling of the bisulphate melt with water or dilute sulphuric acid.

The mineral should be finely ground in agate; the analysis is carried out on 0·25 g., but an accurate colorimetric determination of titania should be made on a separate 0·1-g. portion: this will save time and labour in the analysis of the main portion.

(1) *Determination of titanium.* 0·1000 g. of mineral is fused with 2 g. of potassium bisulphate in a silica crucible, the melt dissolved in 30 ml. of saturated ammonium oxalate solution, and the solution transferred to a beaker, diluted to about 75 ml., and treated with an equal volume of saturated ammonium chloride solution. The earth acids and titania are precipitated

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[1] W. B. Giles, *Chem. News*, 1907, **95**, 1.

[2] C. Marignac, *Ann. Chim. Phys.* (4), 1866, **8**, 5, 49.

with 1·5 g. of tannin and the filtrate tested for complete precipitation exactly as described under **XIII**, § VIII, *a*. The ignited tannin precipitate is once more fused with bisulphate and brought into solution with ammonium oxalate as before; the resultant colourless solution is treated with 25 ml. of 10 per cent. sulphuric acid and hydrogen peroxide, and transferred to a graduated 200-ml. flask, and an aliquot portion (20 or 50 ml.) is tested colorimetrically (§ III, *h*, 2). The standard should contain the same quantities of bisulphate, ammonium oxalate, and acid as the aliquot portion.

(2) *Determination of tantalum and niobium.*[1] (α) 0·25 g. of mineral is fused with 3 g. of potassium bisulphate in a silica crucible. The melt is warmed in the crucible with 15 ml. of 20 per cent. tartaric acid solution until detached, and quantitatively transferred to a squat 250-ml. beaker with 75 ml. of hot water. After addition of 5 ml. of 10 per cent. sulphuric acid, the melt is cautiously dissolved by warming and continuous stirring (§ III, *a*).

(β) The hot solution is treated with hydrogen sulphide until cold, and set aside for some hours to clear; a little creamed filter-pulp stirred into the suspension greatly accelerates settling. The precipitate is collected as prescribed in § III, *a*, 2.

(γ) The filtrate, containing the iron as ferrous salt, is heated to boiling in a 600-ml. beaker and submitted to tartaric hydrolysis (§ III, *c*, 1). The precipitate, HP (major earth-acid fraction), is transferred to a tared silica crucible, and reserved.

(δ) The filtrate from HP is concentrated to 50 ml. in an 800-ml. beaker; the liquid is then quantitatively transferred to a 250-ml. beaker, evaporated on a hot-plate to the consistency of a syrup, diluted to 25 ml., saturated with hydrogen sulphide, and heated with 5 ml. of saturated ammonium chloride solution, excess of ammonia, and a few ml. of ammonium sulphide (§ III, *c*, 2). The precipitate, consisting of ferrous and manganous sulphides, is collected after settling overnight, and washed with ammonium sulphide solution.

(ε) The filtrate from the sulphide precipitate is acidified with hydrochloric acid and boiled in a 600-ml. beaker until hydrogen sulphide is expelled, treated with 3 g. of ammonium oxalate and an equal bulk of saturated ammonium chloride solution, and approximately neutralized with ammonia, a small strip of litmus-paper being added to the solution. The boiling solution is precipitated with 0·5 g. of tannin as under (1), *above*. The precipitate, TP (minor earth-acid fraction and titania), is collected and washed with hot 2 per cent. ammonium chloride solution, the filtrate being tested for complete precipitation by boiling and neutralization (**XIII**, § III, *d*).

The precipitate TP is ignited together with HP and weighed as $(Ta,Nb)_2O_5 + TiO_2$. If tungsten is present in the ore, it is found in this precipitate, which should then be treated by the magnesia method (§ III, *g*, 1). A very subordinate amount (of the order of 0·25 per cent.) of tungstic oxide occurs in some tantalites, but it is usually absent or negligible.

Titania, having been determined in a separate portion (1, *above*), need not be eliminated prior to the separation of tantalum from niobium by the tannin method provided the $Ta_2O_5 : TiO_2$ ratio is well over 50. Hence the same absolute amount of titania causes more pronounced interference in a columbite than in a high-grade tantalite.

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[1] The bracketed Greek letters are used for purposes of reference in § IX on "Complete Analysis."

Operators not too familiar with the tantalum-niobium separation are advised not to omit the separation of the titania unless the $Ta_2O_5 : TiO_2$ ratio exceeds 80. Its removal causes a striking improvement in the vital colour indications. The separation of titania from the earth acids must be effected by the oxalate-salicylate method (§ III, *h*, 3); if the absolute amount of titania present is less than 0·01 g., the double oxalate-salicylate treatment is normally unnecessary.

Finally, the pentoxides, having been freed from titania if necessary, are separated from each other by the tannin process (§ III, *i*). A correction is required if titanium has been separated (§ III, *h*, 3, last paragraph).

(*b*) *Shorter Method for Tantalite* (*Columbite*).—If only tantalum and niobium have to be determined, the shorter tannin precipitation procedure from oxalate solution may be adopted. This is exactly the same as the procedure described for the determination of titania in rutile (**XIII**, § VIII, *a*, 1).

The finely crushed ore (0·25 g.) is fused with 3 g. of potassium bisulphate, and the melt is dissolved in 75 ml. of saturated ammonium oxalate solution. The solution is filtered into a 600-ml. beaker and the residue washed with hot water.

The filtrate is treated as in the titanium analysis referred to, yielding major and minor earth-acid fractions. The combined tannin precipitates are ignited and weighed as a check, then treated (if necessary) for the separation of titania as under (*a*), a separate 0·1-g. portion being used for the colorimetric determination of the titania as in the tartaric acid method. The tannin separation of tantalum from niobium completes the analysis.

(*c*) *In Ferrotantalum* (*Ferroniobium*).—The determination of tantalum and niobium in their ferro-alloys is carried out as in tantalite. The finely divided alloy may be fused with bisulphate, or submitted to acid attack as follows:

The weighed powder (0·25 g.) is covered with hydrofluoric acid in a platinum dish, and strong nitric acid is added cautiously drop by drop while the liquid is being stirred with a platinum rod. The attack takes place in the cold; care must be taken to avoid loss by effervescence. A paraffin-coated clock-glass secured by a clamp may be held over the dish, and later rinsed with cold water. When solution is complete, the dish is gently warmed until the red fumes are expelled; the liquid is treated with 10 ml. of 1 : 1 sulphuric acid and evaporated until white fumes are evolved. The acid is allowed to cool, the sides of the dish are rinsed down with water, and a saturated solution of 5 g. of sodium sulphate is added. The liquid is once more evaporated, and heated more strongly after evolution of sulphuric fumes until a bisulphate melt is left. This is treated by the tartaric acid method (*a*, 2, *a*, *above*); tin, tungsten, and titanium are usually present.

**§ VIII. Determination of Impurities in Ores and Ferro-alloys.**—Niobium has been considered an undesirable constituent of tantalite, not because of any harmful effects, but because it depreciates the grade of the ore, and decreases the yield while increasing the cost of chemicals and labour. If, however, the niobium also is recovered (and this is now being done by the leading producer of tantalum, the metal being added to stainless steels), it figures as a useful if less valuable constituent.

Tin is an undesirable impurity [1] as well as titanium. We have never found any ore entirely free from these two elements. Tungsten also should be tested for. The determination of these impurities in ores as well as ferro-alloys is carried out by the tartaric acid method (§ VII, *a*).

**§ IX. Complete Analysis of Columbite and Tantalite.**—The complete analysis of these ores is conducted by the tartaric acid method, which has been described with sufficient detail in § VII, *a*. What remains to be given here is a brief *résumé* of the operations and the grouping of the constituents effected thereby. For purposes of complete analysis it is desirable to provide an alternative modification of stage (ε), in order to include the determination of the occasional minor constituents zirconia, lime, and magnesia. A 0·5-g. portion of ore may be taken for minor constituents.

The complete analysis of ferro-alloys, involving the determination of tin, tungsten, titanium, tantalum, niobium, and iron, is likewise made by the tartaric acid method.

(α) Fusion with bisulphate, lixiviation with tartaric acid, filtration. Residue: $SiO_2$, $SnO_2$ (§ III, *a*).

(β) *Filtrate from* (α).—Hydrogen-sulphide treatment. Precipitate: $SnS_2$, sometimes a little CuS, rarely $Sb_2S_3$.

(γ) *Filtrate from* (β).—Tartaric hydrolysis. Precipitate: major earth-acid fraction, $WO_3$. Tungstic acid is separated by magnesia method (§ III, *g*, 1); the recovered earth acids are reserved (see ε).

(δ) *Filtrate from* (γ).—Concentration, followed by ammonium-sulphide treatment. Precipitate: FeS, MnS, sometimes a little NiS.

(ε) *Filtrate from* (δ).—Acidification in a 600-ml. beaker with nitric acid and 5 ml. of sulphuric acid, evaporation, and destruction of tartaric acid as usual. The cold mass is taken up with 100 ml. of warm water and 5 g. of ammonium chloride, and the solution precipitated with ammonia. Precipitate: minor earth-acid fraction, titania, zirconia. This is combined with the recovered earth acids from (γ). Separation of earth acids and titania from zirconia: see **XIII,** § VIII, *a*, 1. Separation of titania from earth acids: § VII, *a*, 2. Separation of tantalum from niobium: § III, *i*.

(ζ) *Filtrate from ammonia precipitate* (ε).—Contains CaO, MgO, and possibly traces of MnO.

## XIX.—SELENIUM AND TELLURIUM.

**§ I. Minerals.**—Selenium and tellurium are usually associated in copper ores, which frequently contain small amounts of the elements, selenium predominating over tellurium. Selenium is found in minute amounts in native sulphur, iron pyrites, and stibnite, while tellurium favours gold, silver, lead, and bismuth ores. The rarer minerals listed *below* contain selenium or tellurium as essential constituents.

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[1] Tin may be present in the ore in two forms, *viz.* as mechanically admixed cassiterite, and chemically combined with the earth acids. Cassiterite is hardly attacked in the bisulphate fusion, whilst the combined tin is more or less soluble, the tartrate solution yielding a substantial sulphide precipitate.

(*a*) *Selenium Minerals.*—(1) *Clausthalite*, lead selenide, PbSe, is lead-grey, metallic, and resembles granular galena, with which it is isomorphous. Streak dark grey; cleavage cubic. H. 3; sp. gr. 7·6 to 8·8. In *naumannite*, silver predominates over lead.

(2) *Tiemannite*, mercury selenide, HgSe; dark grey, streak black; isometric. H. 2·5; sp. gr. 8·2.

(3) *Guanajuatite* (*frenzelite*), bismuth selenide, $Bi_2Se_3$; isomorphous with stibnite. Bluish-grey; shining grey streak. H. 2·5; sp. gr. 6·2.

(4) *Berzelianite*, cuprous selenide, $Cu_2Se$; silver-white, shining streak. Sp. gr. 6·7.

(5) *Crookesite*, $(Cu,Tl,Ag)_2Se$. See **XI,** § I.

(6) *Chalcomenite*, hydrous cupric selenite, $CuSeO_3.2H_2O$. Bright blue transparent monoclinic crystals.

(*b*) *Tellurium Minerals.*—(1) *Sylvanite* (*graphic tellurium*), $(Au,Ag)Te_2$, steel-grey to silver-white monoclinic crystals of metallic lustre. H. 1·5 to 2; sp. gr. 7·9 to 8·3.

(2) *Calaverite* contains more gold than sylvanite. Pale yellow. H. 2·5; sp. gr. 9.

(3) *Petzite*, $(Ag,Au)_2Te$, is iron-grey to black; lustre metallic. H. 2·5 to 3; sp. gr. 8·7 to 9·0. As the amount of gold decreases, it graduates into *hessite*, $Ag_2Te$.

(4) *Nagyagite*, perhaps $(Au,Pb)_2(Te,S,Sb)_3$; dark lead-grey colour and streak. H. 1 to 1·5; sp. gr. 6·8 to 7·2.

(5) *Altaite*, lead telluride, PbTe, is tin-white, of metallic lustre, and cubic habit and cleavage. H. 3; sp. gr. 8·2.

(6) *Coloradoite*, mercuric telluride, HgTe; iron-black, metallic appearance. H. 3; sp. gr. 8·6.

(7) *Tetradymite*, bismuth sulphotelluride, $Bi_2(Te,S)_3$; steel-grey hexagonal crystals; marks paper. H. 1 to 2; sp. gr. 7·4.

(8) *Tellurium* occurs native; the crystals are hexagonal, of tin-white streak and colour. H. 2 to 2·5; sp. gr. 6·2.

(9) *Selen-tellurium*, $Te_3Se_2$, is hexagonal, like the preceding. Dark grey, streak black.

(10) *Tellurite* (*telluric ochre*), impure $TeO_2$; yellowish, earthy.

§ **II. Properties and Compounds.**—(*a*) *Selenium* is known in several allotropic modifications analogous to those of sulphur. The red, amorphous or colloidal, variety is produced by the reduction of selenious acid in the cold; it is soluble in carbon disulphide, as is also the vitreous form, obtained by rapid cooling from 217° C. The solution in carbon disulphide deposits red crystalline selenium, which can be obtained in two modifications, both monoclinic, one of which is isomorphous with sulphur. Sp. gr. 4·47; m.p. 170° to 180° C. When fused it rapidly passes over into the black metallic variety, the temperature rising to 217° C., the melting-point of the latter; sp. gr. 4·8; hexagonal, isomorphous with tellurium. B.p. 680° C. The colour of the vapour is dark red, and its density, like that of sulphur vapour, decreases rapidly as the temperature increases. The metallic form conducts electricity, and its conductivity is transiently increased during exposure to light; in the dark, the resistance gradually returns to its former maximum. Nitric acid converts selenium into selenious acid.

(*b*) *Tellurium* may be obtained as an amorphous black precipitate by reduction of tellurous or telluric acid solutions. When heated, it changes into the crystalline variety, which is silver-white and of metallic appearance, but very brittle, closely resembling antimony. Sp. gr. 6·27; m.p. 452° C. It boils at 1390° C., giving a golden-yellow vapour. Insoluble in carbon disulphide. Nitric acid converts it into tellurous acid.

(*c*) The *dioxides*, $SeO_2$ and $TeO_2$, are formed when the elements burn in air or oxygen. They are white crystalline compounds. Selenium dioxide (needle-shaped crystals) is converted at about 300° C. without melting into a greenish-yellow vapour. Tellurium dioxide, which is only very slightly soluble in water, can be fused and sublimed.

(*d*) *Selenious* and *tellurous acids*, $H_2SeO_3$ and $H_2TeO_3$, are formed by the action of nitric acid upon the elements. They are colourless solids: selenious acid crystallizes in large prisms readily soluble in water, whilst tellurous acid is obtained as a voluminous white precipitate when the solution of tellurium in nitric acid (which contains an unstable nitrate) is poured into water, its solubility in water being very slight.

The solution of tellurous acid in hydrochloric acid is reduced by sulphur dioxide, hydrazine, stannous chloride, and zinc, while selenious acid is reduced by the same reagents, as well as by hydriodic acid, hydroxylamine, and ferrous sulphate.

(*e*) *Selenic* and *Telluric Acids.*—Like the preceding, these two acids exhibit a distinct dissimilarity. Selenic acid, $H_2SeO_4$, crystallizes in colourless prisms, which melt at 58° C. It resembles sulphuric acid, having a great affinity for water, with which it forms a monohydrate (m.p. 25° C.). For its preparation, selenium or selenious acid is treated with chlorine in the presence of water:

$$H_2SeO_3 + Cl_2 + H_2O \rightleftharpoons H_2SeO_4 + 2HCl.$$

Telluric acid, $H_2TeO_4.2H_2O$, is prepared from tellurium or tellurous acid by oxidation with nitric and chromic acids, the crystalline mass being purified by solution in water and reprecipitation with nitric acid. The crystals lose water at 160° C., being converted into a white powder of allotelluric acid, $(H_2TeO_4)_n$. This is very slowly soluble in water, producing a solution of the hydrated acid.

For the reduction of selenic and telluric acids, see § III, *a*, 8 and 9. Selenic acid forms selenates, isomorphous with sulphates. Barium selenate, $BaSeO_4$, bears a very close resemblance to barium sulphate, but is reduced and dissolved by boiling with hydrochloric acid. Telluric acid is very feebly acidic, and gives no tellurate alums.

(*f*) The *sulphoxides*, $SeSO_3$ and $TeSO_3$, are formed by solution of the elements in warm concentrated sulphuric acid. The selenium compound forms a green solution, which is decolorized upon addition of water, with precipitation of red selenium. The solution of the tellurium compound in sulphuric acid, which has a fine carmine-red colour, is decolorized by dilution with water, black tellurium being precipitated.

(*g*) *Hydrides.—Hydrogen selenide*, $H_2Se$, and *hydrogen telluride*, $H_2Te$, are colourless, poisonous gases of most offensive odour. They are prepared by the action of hydrochloric acid upon certain selenides and tellurides. Hydrogen selenide gives precipitates of selenides when passed through solutions of heavy metals; it decomposes at 150° C. The properties of hydrogen telluride are similar, but it is much more unstable, decomposing at 0° C.

(*h*) *Sulphides* of selenium and tellurium have not been isolated. Hydrogen sulphide produces a yellow precipitate in selenious acid, and a brown one in tellurous acid, solutions. The precipitates are mixtures of the reacting elements; they are soluble in alkaline sulphide solutions.

(*i*) *Potassium selenocyanate*, KCNSe, is formed when amorphous selenium is dissolved in potassium cyanide solution; hydrochloric acid decomposes the solution, with precipitation of red selenium. Tellurium is insoluble in cyanide solution.

§ **III. Quantitative Separation.**—Within the past twenty years, selenium and tellurium have been harnessed for industrial uses and, at the same time, their analytical chemistry has been thoroughly explored, a task in which American investigators have taken a leading part. Amongst these may be cited V. Lenher, F. A. Gooch, B. L. Browning, and their coworkers. As a result, the factors affecting the accuracy of the determination of the two elements have been elucidated, and reliable methods for their separation worked out.

Since selenium and tellurium occur in minerals in very subordinate quantities, their determination in ores must be conducted in a larger portion of material than those intended for base-metal assays. Active search has been made for traces of selenium on account of its toxic properties. In the manufacture of sulphuric acid, selenium derived from pyrites deposits in the mud which accumulates in the lead chambers. Both elements occur in copper ores, and are ultimately recovered in an enriched form in the anode mud from the electrolytic refining process, along with the precious metals. This sludge is the raw material from which selenium and tellurium are extracted.

The analytical chemistry of selenium and tellurium hinges on the reducibility of their soluble compounds by various reagents, the elements being precipitated as such. In this respect their behaviour is analogous to that of the noble metals. Sulphur dioxide is the most usual precipitant for selenium, while hydrazine is most efficient for the precipitation of tellurium. Potassium iodide is applied in the colorimetric determination of selenium, hydroxylamine in the separation of selenium from tellurium. A systematic procedure, utilizing stannous chloride as reducing agent, has been proposed by the senior author[1] for the determination of small amounts of selenium and tellurium in a variety of materials. Both elements may be determined by volumetric processes based on oxidation or reduction; this subject has been very fully explored.

(*a*) *Properties of Selenium and Tellurium Compounds of Analytical Importance.*—The following is a brief synopsis of the analytically important properties of the two elements and their principal compounds:

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[1] W. R. Schoeller, *Analyst*, 1939, **64**, 318.

(1) The elements form two classes of compounds, derived from the dioxides and trioxides respectively. Of these, the dioxides and their derivatives are of major analytical importance.

(2) Oxidation of the elements and native selenides and tellurides by nitric acid or *aqua regia* proceeds only to the quadrivalent state, giving selenious and tellurous acids.

(3) Selenious and tellurous acids dissolve in hydrochloric acid, giving the tetrachlorides; these are readily reduced by sulphur dioxide or hydrazine in acid solution, elementary selenium and tellurium being precipitated. This reaction is utilized for their gravimetric determination.

(4) Acid solutions of the tetrachlorides are precipitated by hydrogen sulphide; the precipitated sulphides are unstable, dissociating into their elements. The precipitates are soluble in alkaline sulphides.

(5) Selenium tetrachloride is markedly volatile, hence a hydrochloric-acid solution of selenious acid cannot be evaporated, even on a covered water-bath, without serious loss. The addition of sodium chloride does not prevent volatilization. Tellurium tetrachloride, on the other hand, is much less volatile, and its acid solution can be evaporated on a water-bath without risk of loss.

(6) The tetrachlorides can be volatilized quantitatively at higher temperatures.

(7) Oxidation to the sexivalent state (selenic and telluric acids) takes place when the elements or their native compounds are fused with oxidizing alkaline fluxes, or when solutions of selenious and tellurous acids are treated with chlorine.

(8) Selenic and telluric acids are not reduced by sulphur dioxide, and not precipitated by hydrogen sulphide (very slowly in strongly acid solution). They are reduced to the *-ous* acids by boiling with hydrochloric or hydrobromic acid, but this operation is attended by partial volatilization of selenium (5, *above*) and hence has to be conducted under reflux. Hydrazine reduces the *-ic* acids with precipitation of the elements.

(9) Stannous chloride precipitates the elements from hydrochloric-acid solutions of the *-ous* acids in the cold and of the *-ic* acids on heating.

(10) In presence of a large excess of ferric salt, selenious and tellurous acids are occluded in the precipitate produced by ammonia, in the same manner as arsenic and antimony. Selenic and telluric acids are not precipitated on ferric hydroxide; the former is a strong acid resembling sulphuric acid.

(11) Selenium volatilizes when ignited, while tellurium does not.

(*b*) *Interference of Selenium and Tellurium in the Determination of other Metals.*—Selenium and tellurium are said to belong to the second analytical or hydrogen-sulphide group, in which they are assigned to the arsenic sub-group on account of the solubility of the "sulphide" precipitate in ammonium sulphide. However, their inclusion (like that of the earth acids and the platinum metals) in a scheme originally devised for the "common" metals is justifiable only on pedagogic grounds; it is of no practical value, because precipitation of the two elements by hydrogen sulphide is often incomplete, depending on a number of factors, such as acidity and temperature of the solution and the degree of oxidation of the elements; in the treatment of the sulphide precipitate with alkaline sulphide, their behaviour is influenced by association, in that they remain partly or even largely insoluble if copper is present; and the fraction not precipitated by hydrogen sulphide interferes in the treatment of the subsequent groups by contaminating other precipitates in a seemingly capricious manner.

In the analysis of mineral substances containing more than a fraction of one per cent. of selenium *plus* tellurium, the two elements should be removed, prior to the determination of the other constituents, by treatment of the solution with reducing agents. If tellurium (which is much less common and abundant than selenium) is absent, or negligible from the point of view of assaying for other metals, selenium can usually be eliminated by a volatilization method from the portion or portions intended for the determination of the other constituents, with due regard to the possibility of volatilizing certain other elements (*e.g.* arsenic) if present; the selenium determination is carried out in a separate portion of material.

(1) *Elimination of selenium.* (α) *Hydrochloric acid method.* The acid solution is concentrated by evaporation, treated with 5 to 10 ml. of sulphuric and 50 ml. of strong hydrochloric acid, and evaporated on a hot-plate until heavy white fumes are given off. The acid mass is allowed to cool, diluted with a little water, and evaporated with 50 ml. of hydrochloric acid as before. If much selenium is present, a third evaporation may have to be made. The residual liquor is used for the determination of the metals; the method is not applicable to solutions containing arsenious, antimonious, stannic, or mercuric chloride.

(β) *Bisulphate fusion.*[1] A weighed quantity of ore, etc. is fused with potassium bisulphate in a capacious porcelain crucible covered with a watch-glass of the same diameter as the crucible. The fusion is conducted first with a Bunsen, then with a Méker burner, a temperature above 720° C. being required. When the escaping fumes no longer impart a blue colour to the gas-flame, the elimination of selenium is complete. Not applicable to ores containing mercury.

(2) *Elimination of selenium and tellurium.* The following methods are most convenient for the removal of selenium and tellurium from solution prior to the determination of associated elements:

(α) *Reduction of selenious and tellurous acids by sulphur dioxide.* See (*e*), *below.*

(β) *Reduction of selenic and telluric acids by hydrazine and sulphur dioxide.*[2] The ore is dissolved in nitric acid or *aqua regia*, and the liquid evaporated to dryness. The residue is boiled with hydrochloric acid (1 : 1) and the insoluble matter filtered off. The filtrate (150 ml.) is boiled and treated with a current of sulphur dioxide and a few grams of hydrazine hydrochloride; boiling is continued for a few minutes while sulphur dioxide is being introduced. The precipitated elements are filtered off; the filtrate is used for the determination of the base metals.

(*c*) *Elimination of Nitric Acid.*—(1) Nitric-acid attack of ores, slimes, or alloys converts selenium and tellurium into the *-ous* acids (*a*, *above*). The removal of excess nitric acid is effected by evaporation, which must be carried out on a covered water-bath to prevent any loss of selenium by volatilization; the beaker is removed as soon as the residue is dry. Re-evaporation with hydrochloric acid, even with addition of sodium chloride, is inadmissible.

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[1] K. Wagenmann, in *Ausgew. Methoden*, p. 257.

[2] W. W. Scott, *Standard Methods of Chemical Analysis*, 4th edition, 1925, I, 440.

(2) Selenium and tellurium may be recovered from nitric acid or *aqua regia* solutions (which latter should not be evaporated) by precipitation on ferric hydroxide by ammonia (*a*, 10, *above*). The weight of iron present should be at least 30 times that of the selenium *plus* tellurium. The hot, suitably diluted solution is precipitated with a moderate excess of ammonia; the precipitate is allowed to settle, collected on a large filter, and washed with hot water containing a little ammonia and ammonium chloride. If bulky, it is not rinsed back, but the filter is spread out against the side of the beaker and most of the precipitate removed with the glass rod. The last of the precipitate adhering to the paper is dissolved in 1 : 1 hydrochloric acid. This procedure keeps down the bulk of the resultant solution, from which selenium and tellurium are precipitated by stannous chloride (*m*, *below*) or sulphur dioxide (*e*, *below*).

The above ammonia precipitation process can also be applied for the recovery of the two elements from solutions containing large quantities of copper, silver, zinc, nickel, etc. (*g*, 2, *below*).

(*d*) *Separation from Silver.*—(1) The hot acid nitrate solution is treated with a slight excess of hydrochloric acid to precipitate silver chloride, which is collected and determined as usual; the filtrate is treated as under *c*, 2, *above*.

(2) In the presence of large quantities of silver (*e.g.* in the analysis of silver bullion) the acid nitrate solution is precipitated with ferric nitrate and ammonia (*c*, 2, *above*). The precipitate is dissolved in nitric acid, and the precipitation with ammonia repeated.

(*e*) *From Arsenic, Antimony, Tin, Bismuth, and Metals of the Ammonia-Ammonium-sulphide Group: Sulphur Dioxide Method.*—The cold chloride solution, free from nitric acid, is treated with one-quarter to one-third its volume of strong hydrochloric acid, and saturated with sulphur dioxide. Selenium and tellurium are quantitatively precipitated provided they are not present in the sexivalent state. Small amounts of the two elements are slow in settling, hence the solution should not be too dilute, and should be set aside in a warm place or on a covered water-bath until the precipitate has deposited and the supernatant liquid is perfectly clear. This may take a day or more. If no perceptible precipitate is formed, the solution saturated with sulphur dioxide is heated to boiling, left to cool, and again saturated with sulphur dioxide. The precipitate is collected in a porous porcelain crucible and washed with 2 per cent. hydrochloric acid. The filtrate should be tested for complete precipitation by further treatment with sulphur dioxide.

The precipitate produced as described *above*[1] may contain a little antimony and bismuth, and the whole of the gold originally present in the solution. The coprecipitation of antimony may be prevented by addition of tartaric acid prior to sulphur-dioxide treatment; this does not interfere with the precipitation of selenium and tellurium. If much bismuth is present, it may be previously removed more or less completely as oxychloride by partial neutralization and dilution of the solution. Antimony and bismuth can be removed from the precipitated selenium and tellurium by a repetition of the procedure, the washed precipitate being treated with a solution of bromine in strong hydrochloric acid as under *m*, 4, *below*; the solution is diluted with two to three times its volume of water and again saturated with sulphur dioxide (separation of gold: *f*, *below*; of selenium from tellurium: *n*, *below*).

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[1] A. Gutbier (*Zeitsch. anorg. Chem.*, 1902, 32, 263) finds that hydrazine hydrochloride effects a quantitative separation of tellurium from antimony.

The filtrate from the precipitate produced by sulphur dioxide is freed from the gas by evaporation, and the other metals are determined by the usual methods.

(*f*) *From Gold.*—(1) The elements precipitated by sulphur dioxide (*e*, *above*) are digested with hot 1 : 1 nitric acid, selenium and tellurium dissolving. The residual gold is filtered off; the filtrate is evaporated on a covered water-bath for the removal of nitric acid (*c*, *above*), and the residue taken up in hydrochloric acid (80 per cent. by volume) for the separation of selenium from tellurium (*n*, 1, *below*).

(2) In the absence of selenium, gold may be separated from tellurium by treatment of the chloride solution with ferrous sulphate or oxalic acid.

(*g*) *From Copper.*—(1) *Prior to determination of copper by electrolysis.* Selenium and tellurium interfere in the electrolytic precipitation of copper by contaminating the deposit. The copper solution may be freed from selenium by volatilization of the latter from the sulphate solution (*b*, 1, *a*, *above*); from selenium and tellurium by treatment of the hot nitrate solution with excess of potassium hydroxide. The black precipitate of copper oxide is collected, washed with hot water, dissolved in nitric acid, and the solution electrolysed. The filtrate from the copper precipitate may be acidified and treated as under *c*, 2.

(2) *From large amounts of copper.*[1] Small quantities of selenium and tellurium are separated from large amounts of copper by ammonia in presence of ferric salt (*c*, 2, *above*; § VIII, *a*, 1, $\gamma$).

(*h*) *From Lead.*—The nitrate solution, containing sufficient free nitric acid to prevent precipitation of tellurous acid, is precipitated with a moderate excess of sulphuric acid. The lead sulphate precipitate is allowed to settle, collected (under suction if large), and washed with 0·5 per cent. sulphuric acid. The filtrate is treated with a suitable amount of ferric nitrate and precipitated with ammonia (*c*, 2, *above*).

(*i*) *From Mercury.*—(1) *Selenium* is precipitated with ferrous sulphate from the strongly acid chloride solution.

(2) *Tellurium.*[2] The solution is treated with excess of sodium hydroxide, followed by sufficient sodium sulphide to dissolve the precipitate, and boiled with excess of ammonium chloride until the precipitated mercuric sulphide settles. This is filtered off and washed with colourless ammonium sulphide,

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[1] C. Whitehead, *J. Amer. Chem. Soc.*, 1895, **17**, 280.

[2] A. Brukl and W. Maxymowicz, *Zeitsch. anal. Chem.*, 1926, **68**, 14.

then water. The tellurium is precipitated in the filtrate as indicated in § IV, *b*, 3.

(3) *Selenium and tellurium.*[1] The cold dilute solution of the chlorides is treated with phosphorous acid, which precipitates mercurous chloride. The filtrate is treated with sulphur dioxide (*e*, *above*).

(*j*) *From Alkaline Earths, Copper, Iron, etc.: Fusion Method.*—The material is mixed with sodium carbonate and nitrite or nitrate in a platinum crucible, covered with more flux, and heated very gradually, until the mass is fused. The filtered solution of the melt, containing sodium selenate and tellurate, is acidified with hydrochloric acid and precipitated by the hydrazine method (§ IV, *a*, 3).

(*k*) *From Non-volatile Elements.*— Small amounts of selenium and tellurium in the form of native selenides and tellurides may be separated from large quantities of fixed compounds (silicates, etc.) by chlorination. The powder contained in a combustion tube is heated in a current of dry chlorine, the temperature being gradually raised to a dull red and maintained for half an hour. The tube is connected to a receiver containing dilute hydrochloric acid (1 : 2 water), in which the volatilized chlorides condense. Arsenic, antimony, mercury, and bismuth, if present, are also volatilized, and a certain amount of iron. The solution is treated with sulphur dioxide (*e*, *above*).

Ores containing oxidized selenium and tellurium minerals are heated in a current of hydrogen chloride; otherwise the treatment is the same.

(*l*) *From Sulphur.*—(1) The acid chloride solution containing sulphuric, selenious, and tellurous acids is precipitated with barium chloride as usual. The excess of barium in the filtrate is removed by sulphuric acid, and the selenium and tellurium are precipitated by stannous chloride (*m*, *below*).

(2) The same solution is treated with ferric chloride and excess of ammonia (*cf.* *c*, 2, *above*). Selenium and tellurium are precipitated; sulphuric acid passes into the filtrate.

(3) If selenium and tellurium are present in the sexivalent condition, they should be reduced with hydrazine hydrochloride. The acid chloride solution is boiled with 2 or more grams of the salt, under reflux if considered advisable. The filtrate is tested with more hydrazine for complete precipitation, and the sulphuric acid determined as usual.[2] The precipitation of selenium and tellurium by reducing agents is impeded by the presence of much alkali sulphate.

(*m*) *Separation Method utilizing Stannous Chloride.*[3]—Selenium and tellurium may be separated from a large number of elements by precipitation with stannous chloride. The use of this reducing agent for the gravimetric determination of the elements has been condemned on the ground of occlusion of tin in the precipitate[4]; nevertheless it is a valuable, almost specific reagent, by means of which small amounts of selenium and tellurium may be readily isolated from large quantities of other elements. The introduction of tin into the assay solution usually renders the determination of the other elements inconvenient or difficult, hence the stannous chloride method is applied only to the portion (usually a large one, *i.e.* a multiple of 5 g.) intended for the determination of selenium and tellurium. The occlusion of a little tin in the precipitate is immaterial, because the latter is not weighed, but dissolved in brominated hydrochloric acid, and the resultant solution used for the separate determination of the two elements.

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[1] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 8th edition, 1935, **2**, 272.

[2] Dennis and Koller, *J. Amer. Chem. Soc.*, 1919, **41**, 949.

[3] W. R. Schoeller, *Analyst*, 1939, **64**, 318.

[4] Hillebrand and Lundell, *op. cit.*, p. 260, footnote 4.

The determination of selenium and tellurium by the stannous chloride method in a variety of ores, metals, and by-products is described in § VIII, but the general sequence of operations by which the two elements are separated from their associates is given *below*.

(1) *Solution* is effected, whenever possible, by nitric acid only, as oxidation proceeds only to the quadrivalent state, and the risk of volatilizing selenium is avoided. If *aqua regia* or hydrochloric acid is applied, a flask provided with a reflux condenser is safest. Minerals insoluble in acids are fused with sodium peroxide; for clayey or siliceous ores, Kjeldahl digestion is useful (§ VIII, *a*, 1, $\epsilon$).

If nitric acid alone is used, the excess may be evaporated in a beaker on a covered water-bath just to dryness (*c*, 1, *above*); in this case, step (2) need not be applied. If a peroxide fusion has been made, step (2) must not be applied, as selenic and telluric acids are not precipitated on ferric hydroxide; the hydrochloric acid solution of the melt is treated as under (3).

(2) *Precipitation on ferric hydroxide.* If the material is high in copper this step is essential, and it may also be employed instead of evaporation for the removal of nitric acid. The acid liquid obtained as under (1) is diluted and the solution filtered from the insoluble residue; or the residue from the nitric acid evaporation is taken up in hydrochloric acid (1 : 2 water) and the solution filtered. The filtrate is diluted and treated with a suitable quantity of ferric nitrate (*c*, 2, *above*) and excess of ammonia. The precipitate is collected, washed, returned to the beaker as described under *c*, 2, and dissolved in hydrochloric acid (1 : 1).

(3) *Precipitation with stannous chloride.* The solution of the iron precipitate in hydrochloric acid is stirred and treated with a freshly prepared 20 per cent. solution of stannous chloride in hydrochloric acid (about 1 : 2 water). The solution is first decolorized, the iron being reduced to the ferrous state; continued addition of reagent produces a pale reddish-brown, brown, or brownish-black coloration, and on standing the solution becomes practically colourless, with deposition of a reddish to black precipitate containing the whole of the selenium and tellurium. The separation from bismuth, antimony, and arsenic is complete, the hydrochloric acid concentration not being high enough to cause precipitation of arsenic as in Bettendorf's reaction; the precipitate may occlude a little tin, and copper if this metal is present. Although the great bulk of the copper has been removed in step (2), enough of it is left in the ferric hydroxide to combine with the selenium (tellurium) in accordance with the reaction:

$$SeCl_4 + 2CuCl_2 + 4SnCl_2 = Cu_2Se + 4SnCl_4.$$

This is rather an advantage, as the selenide (telluride) precipitate is flocculent and deposits more readily than the pulverulent precipitated elements; and the amount of copper carried down is too small to interfere in the subsequent precipitation with sulphur dioxide.

(4) *Treatment of precipitate produced by stannous chloride.* This is collected on a smallish filter-pad lightly pressed into the apex of the funnel, completely transferred to the filter with N. hydrochloric acid containing a little stannous chloride, washed with the same solution, and finally a few times with 2 per cent. acid. The funnel is then covered with a watch-glass, and the precipitate treated with a solution of bromine in strong hydrochloric acid added drop by drop through a glass tube, the filtrate being received in a small conical flask. The dropwise addition of brominated acid is continued at intervals until the precipitate has dissolved; an excess should be avoided. Finally the filter-pad is washed with small portions of hydrochloric acid (80 per cent. by volume). The filtrate is ready for the separation of selenium from tellurium (*n*, 1, *below*).

(*n*) *Selenium from Tellurium.*—(1) *By sulphur dioxide.*[1] This is the method most commonly applied in metallurgical analysis. It consists in saturating the cold, strongly acid solution of the tetrachlorides with sulphur dioxide, red selenium being precipitated. The concentration of the hydrochloric acid is a vital factor in the separation: the solution should contain at least 80 per cent. by volume of strong acid. Black tellurium is precipitated by sulphur dioxide when the acidity is reduced to one-half of that value—40 per cent. by volume.

Lenher and Kao[2] carry out the process in cold concentrated hydrochloric acid; the concentration of the selenium and tellurium should not exceed 0·25 g. per 100 ml. They precipitate the selenium with a saturated solution of sulphur dioxide in strong hydrochloric acid during continuous agitation. The red precipitate is allowed to settle, collected on a Gooch or porous porcelain crucible, washed with cold strong hydrochloric acid, and in succession with cold water, alcohol, and ether; the precipitate is dried for 3 to 4 hours at 30° to 40° C. and finally at 120° C. for 1 to 2 hours, and weighed.

The filtrate, containing the tellurium, is evaporated to 50 ml. and treated by Lenher and Homberger's method (§ IV, *b*, 1).

(2) *Distillation method.*[3] This is based on the fact that selenium is quantitatively volatilized when a solution of the elements in strong sulphuric acid is treated at 300° to 330° C. with a current of dry hydrogen chloride, whereas tellurium remains wholly behind. The results obtained are excellent, but the process requires a fairly elaborate distillation train, which is a practical disadvantage unless it is applied regularly.

It is usually necessary to separate the two elements from the other constituents as a mixed precipitate which is collected on an asbestos filter. This is introduced with 30 to 60 ml. of strong sulphuric acid into the distillation flask forming part of an all-glass apparatus. Dry hydrogen chloride is passed through the acid; when the air has been displaced, the flask is heated to just below the boiling-point of the acid, the gas current and temperature being maintained for 3 to 5 hours. The escaping gas is led into a cooled receiver containing water through which sulphur dioxide is forced, the selenium being precipitated and determined as under § IV, *a*, 1.

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[1] E. Keller, *J. Amer. Chem. Soc.*, 1897, **19**, 771.

[2] V. Lenher and C. H. Kao, *ibid.*, 1925, **47**, 769.

[3] V. Lenher and D. P. Smith, *Ind. Eng. Chem.*, 1924, **16**, 837.

The residual acid liquor is transferred to a beaker, diluted, filtered, and treated with ferric chloride and an excess of ammonia (*m*, 2, *above*), or neutralized with ammonia, treated with one-quarter its volume of strong hydrochloric acid, and the tellurium precipitated with hydrazine and sulphur dioxide (§ IV, *b*, 1).

(3) *By hydroxylamine.*[1] The solution of the tetrachlorides, which must contain 40 to 45 per cent. by volume of strong hydrochloric acid, is heated to 90° C. for 4 hours after addition of 10 ml. of a 25 per cent. solution of hydroxylamine hydrochloride. The selenium, which is precipitated as the black modification, is collected, washed with water, then with alcohol, dried at 110° C., and weighed. The tellurium in the filtrate is precipitated as in § IV, *b*, 1.

(4) *By precipitation of tellurium dioxide.*[2] The slightly acid solution of the chlorides (obtained by dissolving the elements in nitric acid, evaporating on the water-bath, and dissolving the residue in a little hydrochloric acid) is diluted to 200 ml. with boiling water, made slightly ammoniacal, and barely acidified with acetic acid, tellurium dioxide being precipitated. The solution is set aside till cold and filtered through a tared porous porcelain crucible. The precipitate is washed with warm water, dried at 105° C. (or gently ignited), and weighed as $TeO_2$.

§ **IV. Gravimetric Determination.**—(*a*) *Selenium* is always weighed as the element. The weighing is carried out in a porous porcelain crucible; the selenium is then volatilized by ignition, and the crucible again weighed, the difference giving the weight of the selenium.

The element is rather inert to nitric acid, and can be quantitatively recovered by sulphur dioxide precipitation after slightly incomplete removal of that acid[3]; hence there is no need for repeated or even a single evaporation with hydrochloric acid after nitric acid attack. The evaporation would lead to loss by volatilization (§ III, *a*, 5), but nitric acid may be removed by slow evaporation (*e.g.* on a covered water-bath: § III, *c*, 1).

(1) *By sulphur dioxide.* It should be borne in mind that the precipitation of selenium by sulphur dioxide is subject to certain errors. The temperature of the solution should be kept between 15° and 22° C.[4]: below 15° C. the precipitation is delayed, while above 22° C. the precipitate agglomerates (like sulphur) and occludes impurities, *e.g.* bromine and tellurium, which cannot be removed by washing, and water.

The solution of selenious acid in fairly concentrated hydrochloric acid (50 to 80 per cent. by volume) is treated at the prescribed temperature with a slow current of sulphur dioxide; precipitation readily takes place, and is complete when the solution smells strongly of the gas. The precipitate is allowed to settle in the cold, leaving the solution clear. With minute quantities this may require settling overnight. The precipitate is transferred to a porous porcelain crucible, washed with hydrochloric acid of the same concentration as the solution from which the precipitate was obtained, then with hot water, and finally with alcohol, dried at 105° C., and weighed. The crucible is then heated to redness, the selenium volatilizing with a characteristic smell as of putrid horse-radish. After cooling, the crucible is weighed, and the quantity of selenium found by the loss in weight.

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[1] V. Lenher and C. H. Kao, *J. Amer. Chem. Soc.*, 1925, **47**, 2454.

[2] P. E. Browning and W. R. Flint, *Amer. J. Sci.* (4), 1909, **28**, 12.

[3] K. Wagenmann, in *Ausgew. Methoden*, p. 254.

[4] V. Lenher, in W. W. Scott's *Standard Methods of Chemical Analysis*, 4th edition, 1925, **1**, 435.

(2) *By hydroxylamine.* This has been discussed in § III, *n*, 3.

(3) *By hydrazine.* Solutions containing either nitric acid, or the selenium in the form of selenate, are conveniently treated as follows[1]: A faint excess of ammonia is added to the solution, which is then slightly acidified with hydrochloric acid, and treated with excess of hydrazine sulphate. The covered beaker or flask is heated, boiling being continued until the precipitated selenium becomes dark and settles readily; a little hydrazine salt is added now and again during the boiling. The precipitate is treated as under (1), *above* (except that it need not be washed with hydrochloric acid), and the filtrate tested for complete precipitation by boiling with a further portion of hydrazine salt.

(*b*) *Tellurium* is weighed either as such in a tared porous porcelain or Gooch crucible or on a tared filter; or as the dioxide, $TeO_2$, after gentle ignition in a tared porcelain crucible. Precipitated tellurium oxidizes more readily than selenium, and must be washed with dispatch.

(1) *By hydrazine and sulphur dioxide.*[2] This process may be applied to solutions of tellurous or telluric acid, or in the presence of tartaric acid or hydroxylamine, and precipitation is rapid provided the tellurium concentration is not too low.

The solution, containing one-quarter of its volume of concentrated hydrochloric acid, is heated to boiling and treated successively with 15 ml. of saturated sulphur dioxide solution, 10 ml. of a 15 per cent. solution of hydrazine hydrochloride, and again 25 ml. of sulphur dioxide solution. Boiling is continued until the precipitate of tellurium settles readily (about 5 minutes), after which it is collected in a tared crucible, washed with hot water till free from acid and then with alcohol, dried at 100° to 105° C., and weighed.

(2) *By sulphur dioxide or hydrazine.* The older procedure of precipitating tellurium by sulphur dioxide is not so efficient as the *above*. Precipitation is slow and not always complete, especially in more dilute solutions; the precipitate, being finely divided, does not settle quickly, and is prone to oxidize on the filter. Sulphates interfere with the precipitation.[3]

Hydrazine hydrochloride by itself is a more effective precipitant than sulphur dioxide, but the procedure utilizing the two reagents described under (1), *above*, gives the best results and should be applied whenever possible.

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[1] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 8th edition, 1935, **2**, 268.

[2] V. Lenher and A. W. Homberger, *J. Amer. Chem. Soc.*, 1908, **30**, 387.

[3] L. Moser and R. Miksch, *Monatsh.*, 1923, **44**, 345.

(3) *By sodium sulphite.*[1] The solution of tellurium in sodium sulphide is precipitated by sulphite:

$$Na_2TeS_4 + 3Na_2SO_3 = 3Na_2S_2O_3 + Na_2S + Te.$$

The filtrate obtained in the separation of mercury (§ III, *i*, 2) is boiled for 10 to 20 minutes with 25 ml. of saturated sodium sulphite solution, whereby the yellow colour is discharged, with precipitation of the tellurium. Boiling is continued until the precipitate flocculates, when the liquid is diluted to 250 ml. and boiled with a little more sulphite. The precipitate is left to settle, collected in a tared porous crucible, washed with hot water, alcohol, and ether, dried for a short time, and weighed.

(4) *As tellurium dioxide.* The precipitation of the dioxide has been described under § III, *n*, 4; the precipitate is weighed after having been dried at 105° C., or gently ignited.

Tellurium precipitated by one of the methods (1) to (3) may be converted into and weighed as dioxide. The precipitate is dissolved in nitric acid (1 : 2 water) containing a few drops of sulphuric acid. The solution is evaporated to dryness in a tared porcelain crucible or small dish, and the residue gently ignited and weighed.

§ **V. Volumetric Determination.**—Although a large number of volumetric methods for the determination of the two elements have been worked out, they do not appear to have displaced the gravimetric processes in actual practice. This may be due to the fact that tellurium interferes in all selenium titrations, and *vice versa* (with one exception, *b*, 1, *below*); hence the elements must first be isolated, in which case it is really simpler to weigh them. A selection of reliable procedures is given *below*:

(*a*) *Selenium.*—(1) *Thiosulphate method.*[2] Selenious acid reacts with sodium thiosulphate, forming selenopentathionate:

$$H_2SeO_3 + 4Na_2S_2O_3 + 4HCl = Na_2SeS_4O_6 + Na_2S_4O_6 + 4NaCl + 3H_2O.$$

The solution is diluted with ice-water, treated with 10 ml. of hydrochloric acid (sp. gr. 1·12) and a measured excess of 0·1N. thiosulphate solution, and set aside for 24 hours, after which the excess of thiosulphate is measured with 0·1N. iodine. The iodide contained in the iodine solution must be free from iodate, and the thiosulphate solution free from sulphite, *i.e.* it should consume the same amount of iodine in acid as in neutral solution. 1 ml. of 0·1N. iodine solution is equivalent to 0·002774 g. of $SeO_2$. The results obtained are highly concordant.

(2) *Iodimetric determination.*[3] Selenious acid reacts with iodide in acid solution according to the equation:

$$SeO_2 + 4HI = Se + 2H_2O + 2I_2.$$

The volumetric determination of the liberated iodine gives low results because it is in part adsorbed by the selenium precipitate. The following process avoids this drawback: the selenite solution is diluted in a glass-stoppered flask to 100 ml. and acidified with 10 ml. of 25 per cent. hydrochloric acid. Carbon disulphide (30 ml.) is added, then 1·5 times the required quantity of 0·2N. potassium iodide in a thin stream while the flask is given a rotatory motion. After one minute's vigorous shaking, the iodine is titrated with thiosulphate, the liquid being well shaken after each decolorization of the aqueous layer, and starch solution used towards the end. 1 ml. of 0·1N. thiosulphate $\equiv$ 0·001974 g. of selenium.

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[1] A. Brukl and W. Maxymowicz, *Zeitsch. anal. Chem.*, 1926, **68**, 14. O. E. Clauder (*ibid.*, 1932, **89**, 270) recommends potassium hypophosphite as an efficient precipitant for tellurium.

[2] J. F. Norris and H. Fay, *Amer. Chem. J.*, 1896, **18**, 703; 1900, **23**, 119.

[3] R. Berg and M. Teitelbaum, *Chem. Zeit.*, 1928, **52**, 142.

(*b*) *Tellurium.*—(1) *Dichromate method.*[1] Selenium does not interfere with the determination. The solution of tellurous acid in 15 ml. of strong hydrochloric acid is diluted to 200 ml., treated with a measured excess of 0·1N. dichromate, and set aside for half an hour, after which a slight excess of 0·1N. ferrous sulphate solution is added. The excess of ferrous salt is then titrated with 0·1N. dichromate after addition of sulphuric and phosphoric acids and 3 drops of a 1 per cent. solution of diphenylamine in strong sulphuric acid. The difference between the total volume of the dichromate and that of the ferrous salt solution gives the dichromate consumed by the tellurous acid:

$$2CrO_3 + 3TeO_2 = Cr_2O_3 + 3TeO_3.$$

1 ml. of 0·1N. $K_2Cr_2O_7 \equiv$ 0·006381 g. of tellurium.

(2) *Iodimetric determination of telluric acid.*[2] The direct reduction of telluric acid by iodides does not give concordant results, but with bromides the reaction proceeds uniformly, thus:

$$TeO_3 + 2HBr = TeO_2 + H_2O + Br_2.$$

The tellurate solution is distilled with 3 g. of potassium bromide, and 10 ml. of sulphuric acid (1 : 1) per 50 ml. bulk. Two receivers placed in series contain a solution of 3 g. of potassium iodide; the first is placed in cold water. The distillation is continued until the volume of the liquid has been reduced to 20 ml.; the last of the bromine is expelled by a current of carbon dioxide. There should be no rubber connection between the distilling flask and the first receiver. The iodine in the distillate is titrated with 0·1N. thiosulphate, 1 ml. of which $\equiv$ 0·008781 g. $TeO_3$.

(*c*) *Selenium and Tellurium: Permanganate Titration.*[3]—This process can be applied without modification to selenium, or tellurium, or both together. The solution of selenious (tellurous) acid in 25 ml. of 40 per cent. sulphuric acid is diluted to 150 ml., and treated with 12 g. of crystallized sodium phosphate (which prevents precipitation of manganese dioxide) and a measured excess (of at least 10 ml.) of 0·1N. permanganate. After half an hour's standing the excess of permanganate in the solution is titrated with 0·1N. ferrous sulphate solution. Chlorides must be absent. 1 ml. of 0·1N. $KMnO_4 \equiv$ 0·003948 g. of selenium or 0·006381 g. of tellurium.

§ **VI. Colorimetric Determination.**—No colorimetric methods for tellurium appear to have been published, but several processes have been proposed for selenium. These are based upon conversion of selenious acid into colloidal selenium by means of a reducing agent and comparison of the reddish tint of the suspension with that obtained with a standard solution of selenious acid.

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[1] V. Lenher and H. F. Wakefield, *J. Amer. Chem. Soc.*, 1923, **45**, 1423.
[2] F. A. Gooch and J. Howland, *Amer. J. Sci.* (3), 1894, **48**, 375.
[3] W. T. Schrenk and B. L. Browning, *J. Amer. Chem. Soc.*, 1926, **48**, 2550.

The method of Meyer and von Garn[1] utilizes potassium iodide (*cf.* § V, *a*, 2), which has the advantage that the colour of the selenium suspension is intensified by the liberated iodine. Five ml. of the solution under investigation, and a similar volume of a standard solution, are transferred to Nessler tubes provided with a stopcock near the bottom. To each cylinder are added 70 ml. of purest distilled water, one drop of protective colloid (gum arabic), and 5 ml. of 5 per cent. hydrochloric acid. After making up to 99 ml. and stirring well, 1 ml. of 50 per cent. potassium iodide is mixed in, the tints being matched after five minutes' standing by withdrawing a suitable quantity of liquid from the tube in which the colour is strongest, into a measuring cylinder. 0·0001 g. of $SeO_2$ can thus be determined in 100 ml. of solution.

A slightly different technique for the colorimetric determination of selenium is described in § VIII, *a*, 1, $\theta$.

§ **VII. Detection in Ores.**—Before discussing the detection of selenium and tellurium in ores, we will enumerate their specific reactions:

(*a*) *Specific Selenium Reactions.*—(1) A particle of a mineral or a precipitate of selenium, heated on charcoal in the reducing flame, emits fumes of a penetrating odour, commonly compared to that of putrid horse-radish or rotten cabbage. Precipitated selenium, when ignited in a crucible, volatilizes with the same disagreeable smell.

(2) The most characteristic wet selenium reaction is the formation of a bright red precipitate in a cold, strong hydrochloric-acid solution upon introduction of sulphur dioxide. This is given by selenious, but not by selenic, acid. A solution of selenic acid in hydrochloric acid should first be heated, when reduction to selenious acid takes place. When cool, the reduced solution will yield the red precipitate with sulphur dioxide. When a hot solution of selenic acid in hydrochloric acid is treated with sulphur dioxide, the black modification of selenium is precipitated: this may be mistaken for tellurium, but its deportment in reactions (3) and (4) is a certain proof of its identity.

(3) Selenium is soluble in warm strong sulphuric acid with a green colour. When the cold green solution is poured into cold water, the red modification of selenium is precipitated (distinction from tellurium: *cf. b*, 3).

(4) Selenium is soluble upon digestion in potassium cyanide solution (distinction from tellurium). The colourless solution, which contains selenocyanate, is decomposed by excess of hydrochloric acid, with precipitation of red selenium.

(5) Selenious acid solutions are reduced by potassium iodide and by ferrous sulphate, with precipitation of selenium (distinction from tellurium).

(*b*) *Specific Tellurium Reactions.*—(1) A hot solution of tellurous acid in moderately strong hydrochloric acid (about 1 : 2 water—*cf.* § III, *n*, 1) gives a black precipitate upon treatment with sulphur dioxide, more readily after addition of a little hydrazine hydrochloride. For the certain detection of tellurium in the form of telluric acid, the hydrochloric-acid solution is treated with hydrazine hydrochloride, boiled, and saturated with sulphur dioxide.

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[1] *Zeitsch. anal. Chem.*, 1914, **53**, 29.

It is always advisable to test the black precipitate by reaction (3).

(2) Stannous chloride produces in cold, moderately acid chloride solutions of tellurous acid an intense black precipitate, or coloration if the solution is rather dilute, in which case flocculation sets in sooner or later. Telluric acid solutions in moderately strong hydrochloric acid give the same reaction when heated with stannous chloride. The black precipitate should be tested by reaction (3).

*Note.*—Stannous chloride should not be added to solutions containing sulphurous acid, as it gives a precipitate of stannous sulphide.

(3) The following tellurium reaction is absolutely specific, as well as sensitive, and should always be carried out: The black precipitate obtained under (1) or (2) (or a picked particle of a telluride mineral) is warmed in a porcelain crucible with a little strong sulphuric acid, which dissolves it, thereby acquiring a fine carmine colour. When the cold acid is diluted with water the colour is discharged, and black tellurium precipitated.

Tellurium dioxide (§ IV, *b*, 4)—or oxidized tellurium minerals—yield the same carmine coloration when a small piece of tin-foil is added to the hot sulphuric acid. Iron, if present, interferes with the test.

(*c*) *Detection of Selenium and Tellurium in Ores.*—(1) *By chlorination.* Ores poor in selenium and tellurium may be heated in a chlorine current in a glass combustion tube, the drawn-out end of which dips into dilute hydrochloric acid. The heat is applied for about an hour, gently at first, later at dull redness, after which the acid solution is saturated with sulphur dioxide and set aside overnight if necessary. Alternatively the solution may be reduced with stannous chloride. In either case the precipitate is treated as under (5), *below.*

(2) *Fusion method.* The powdered mineral is fused with an alkaline oxidizing flux, either sodium carbonate and nitrite (preferable to nitrate, as the resultant solution will be free from nitric acid) or sodium peroxide. The cold melt is taken up in hot water and the liquid set aside till clear or nearly so. The clarified portion is decanted off, acidified with hydrochloric acid, and boiled for the removal of nitrous fumes if nitrite was used as a flux. The boiling-hot solution is treated with one-quarter of its volume of strong hydrochloric acid and an excess of stannous chloride (§ III, *m*, 3). The precipitate is allowed to flocculate, and treated as under (5), *below.*

(3) *Acid attack.* The material is decomposed with nitric acid or *aqua regia*; when attack is complete the acid is diluted and, if much lead is present, the bulk of it is precipitated with dilute sulphuric acid. The insoluble portion is filtered off, and the filtrate treated with 0·2 g. of iron as ferric nitrate unless sufficient iron is judged to be present. The hot solution is precipitated with ammonia, the precipitate collected, washed a few times, dissolved in hydrochloric acid (1 : 1), and the solution treated with excess of stannous chloride, etc., as under (2), *above.*

(4) *Pot fusion.*[1] The ore (*e.g.* gold-telluride ore) is submitted to fusion

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[1] G. T. Holloway and L. E. B. Pearse, *Trans. Inst. Min. Met.*, 1908, 17, 175.

with litharge, flour, and fluxes in a clay crucible, as in the dry gold assay. The cleaned lead button is dissolved in dilute nitric acid, the filtered solution diluted, and a bright strip of lead foil inserted. Any black deposit is dried, rubbed off, and heated with sulphuric acid and tin foil (*b*, 3, *above*). Alternatively, the nitrate solution is treated with enough ammonia to produce a slight precipitate. The latter, which contains the bulk of the tellurium, is collected, washed, dried, and heated with concentrated sulphuric acid and tin foil.

(5) *Separate identification of selenium and tellurium.* The precipitate obtained as under (1) to (3), *above*, is collected on a small pad of filter-pulp, washed a few times with 2 per cent. hydrochloric acid, and dissolved by dropwise addition of a solution of bromine in concentrated hydrochloric acid. The filtrate is caught in a small conical flask, the filter washed with hydrochloric acid (80 per cent. by volume), and the liquid treated with a slow current of sulphur dioxide. When the bromine colour has been discharged, the formation of a red precipitate proves the presence of selenium. The introduction of the gas is continued until the precipitation of selenium is complete. The precipitate is collected on a pad of filter-pulp, the filtrate diluted with an equal volume of water, boiled, and treated with hydrazine hydrochloride. The black precipitate is left to settle, most of the clear liquid poured off and rejected, and the suspension filtered through a small asbestos pad. This is washed with water, then with alcohol, dried, and warmed in a porcelain crucible with a few drops of strong sulphuric acid. A carmine coloration proves tellurium to be present.

§ **VIII. Determination in Ores.**—Selenium and tellurium normally occur in very subordinate quantities in metalliferous minerals. With few exceptions,[1] base-metal ores contain less than 0·1 per cent. of selenium if any, and usually less tellurium than selenium. However, tellurium favours gold, bismuth, and lead ores; selenium, copper and antimony ores and pyrites. From the practical point of view it is convenient to consider the determination of the two elements under two heads: (*a*) the ore contains small quantities of selenium and tellurium; and (*b*) the material carries more substantial quantities of the two elements.

(*a*) *Ores Containing Small Quantities of Selenium and Tellurium.*—Unless the material is refractory to acids, the fusion method given under (2), *below*, is of limited usefulness, since a large amount of ore must be taken; this requires considerable flux and a crucible of inconvenient size,[2] or a number of crucibles. The chlorination method described *below* is not recommended for substantial quantities of rich sulphide or pyritic ores, because the whole of the sulphide mineral must be chloridized, all the sulphur and much iron volatilizing.

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[1] By far the richest seleniferous ore deposit appears to be the Boliden Mine in the Skellefteå district of N. Sweden; it is also the most extensive deposit of arsenical ore. Villamaninite, $(Cu,Ni,Co,Fe)(S,Se)_2$, first identified by the authors as a new mineral species (*Min. Mag.*, 1920, **19**, 14), is fairly abundant in one locality in N. Spain, and contains up to 1·5 per cent. of selenium.

[2] The only method given in *Ausgew. Methoden* (p. 258) for the determination of selenium in pyrites and copper matte involves fusion with sodium peroxide, 100 g. of material being fused with 400 g. of peroxide in a stout iron crucible 16 cm. high; a burning match introduced into the charge is the only safe way to start the reaction. We consider the procedure as unattractive as it is unnecessary; nitric-acid attack answers quite well.

Whenever possible, we recommend acid attack as being simplest in the case of large assay portions, especially when applied in conjunction with the stannous chloride method for recovering the two elements prior to their separation. Moreover, acid attack answers best in the very case where the other two processes are inconvenient, namely, with rich sulphide ores.

(1) *Acid attack.* General directions for effecting solution, recovering selenium and tellurium from the solution by stannous-chloride precipitation, and separating them from each other, have already been given in § III under the following heads: (*m*, 1), solution; (*m*, 2), precipitation on ferric hydroxide; (*m*, 3), precipitation with stannous chloride; (*m*, 4), treatment of precipitate produced by stannous chloride; and (*n*), separation of selenium from tellurium.

It remains to describe the application of this procedure to ores, metals, and by-products in which the determination of the two elements is often required.

(α) *Selenium in pyrites.*[1] This is the most common and important case occurring in practice; the stannous chloride method has been applied to it for several years.

The finely powdered ore (10 to 20 g.) is treated in a 2000-ml. beaker with strong nitric acid (60 to 120 ml.). When the first violent action is over, the covered beaker is gently heated; a vigorous action must be kept up, but the heat should not be raised to the melting-point of sulphur, as the larger globules retain selenium and are difficult to attack. Finally the clock-glass is removed, and the red fumes are allowed to escape. The acid solution is diluted with warm water and the solution passed through a loose filter. Should any but small particles of sulphur remain unattacked, the filter containing them must be dried, the sulphur collected and crushed, and oxidized with fuming nitric acid, the resultant solution being added to the bulk. The warm solution (1000 to 1500 ml.) is made ammoniacal and set aside on a water-bath for a short time; the precipitate is collected on a 24-cm. filter and washed a few times with hot water, care being taken to gather the ferric hydroxide into a compact mass, which is left to drain and can then be scooped out with a split clock-glass or porcelain spoon, returned to the beaker in which the precipitation was made, and the remainder dissolved off the paper with 1 : 1 hydrochloric acid. The acid solution is reduced with stannous chloride, etc.

Copper sulphide ores and mattes may be treated in the same manner as pyrites.

(β) *Selenium in stibnite, liquated sulphide, and antimony metal.* In this case, ammonia precipitation on ferric hydroxide is unnecessary. The fine powder (5 g.) is oxidized with 40 ml. of strong nitric acid; when attack is complete the beaker is uncovered, placed on a covered water-bath, and the acid is evaporated just to dryness. The cold dry mass is cautiously treated with 40 ml. of hydrochloric acid (4 : 1 water), added in portions while the beaker is being kept cool. The clear solution is diluted with 50 ml. of water, cooled, and the selenium precipitated with excess of 10 per cent. stannous chloride solution. If necessary, the precipitates from several 5-g. portions are combined. Stibnite ores and antimony may also be treated by fusion with peroxide (2, *below*).

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[1] W. R. Schoeller, *Analyst*, 1939, **64**, 318.

($\gamma$) *Crude and refined copper.* Fifty g. of drillings are dissolved in 200 ml. of nitric acid added in portions, the first portion being diluted. Any sulphur remaining undissolved, or any dark residue (which may contain silver selenide), must be collected and treated with fuming nitric acid. The nitrate solution is treated with a solution of 0·5 g. of iron in nitric acid, and excess of ammonia; the precipitate is collected, washed, dissolved in hydrochloric acid, and the precipitation with ammonia repeated. From this point onward the general procedure is followed.

($\delta$) *Tellurium in lead and galena.* Twenty g. (or more) is dissolved in 150 ml. of hot 25 per cent. nitric acid. The lead is precipitated with excess of dilute sulphuric acid, the lead sulphate collected under slight suction, and washed with 5 per cent. sulphuric acid. The filtrate is treated with 0·3 to 0·5 g. of iron in nitric acid solution, and then with a slight excess of ammonia, the ferric hydroxide collected, washed, and worked up as indicated.

When a gold ore is smelted with litharge and fluxes, any tellurium present passes into the lead button, and is determined therein by the above method.

($\epsilon$) *Oxide ores, etc.* Oxidized material (iron ores, calcined blende, etc.), if attacked with hydrochloric acid, must be heated in a flask fitted with a reflux condenser. Clayey or siliceous ores treated in this manner may give trouble in the filtration of the insoluble due to colloidal silica, since the volatility of selenium precludes evaporation to dryness. If such ores are fused with sodium peroxide the amount of material is limited by the capacity of the crucible, and gelatinous silica may still interfere in the subsequent operations. In such cases decomposition with strong sulphuric acid is applied. Twenty g. of ore is introduced into a 500-ml. Kjeldahl flask, and boiled with 50 ml. of sulphuric acid. The cooled acid is cautiously diluted with 50 to 75 ml. of water, 30 ml. of strong nitric acid added, and the flask again heated for some time. The cooled contents are transferred to a beaker, diluted, and filtered from insoluble matter. The filtrate is precipitated with ammonia, ferric nitrate having been added if necessary.

The Kjeldahl digestion method is applied in the search for selenium in soils.[1]

($\zeta$) *Electrolytic sludge.* Cupriferous anode slimes (1 g.) containing up to 3 per cent. of selenium and about 0·5 per cent. of tellurium are digested with 25 ml. of strong nitric acid in a conical flask. The solution is diluted, filtered, treated with a solution of 1 to 2 g. of iron in nitric acid, and precipitated with ammonia; the precipitate is collected, dissolved, and reprecipitated. The subsequent treatment is the same as in the preceding cases, except that the precipitate produced by stannous chloride is digested with the brominated acid in a flask instead of on the filter. In this manner a more protracted attack is ensured, and less bromine is required. The resultant solution is diluted with one-quarter of its volume of water, filtered through pulp, and the filtrate precipitated with a slow current of sulphur dioxide, etc.

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[1] M. J. Horn, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 34.

(η) *Chamber mud* is extracted with water, and the residue digested with ammonium carbonate solution. The lead carbonate thus obtained is collected, dissolved in dilute nitric acid, the solution decanted, and the residue digested with stronger acid. The lead nitrate solution is precipitated with sulphuric acid (*cf.* δ, *above*), and the lead sulphate filtered off and rejected. All the extracts and filtrates are combined, acidified if necessary, treated with ferric nitrate solution, and precipitated with ammonia, etc.

(θ) *Selenium in sulphur.*[1] The powdered sulphur (5 g.) is added in small portions to 100 ml. of fuming nitric acid (sp. gr. 1·5, strength 94 per cent.) at such a rate that a vigorous action is maintained. When attack is complete the nitric acid is evaporated until fumes of sulphuric acid begin to appear. The cold acid is diluted to 85 ml., filtered into a 150-ml. beaker, cooled, treated with 10 ml. of 10 per cent. potassium iodide, and 1 ml. of a 5 per cent. solution of gum arabic, and placed for 15 minutes in an oven at 55° to 60° C. The liquid is then cooled, treated with a drop of starch solution, the blue colour discharged with sulphurous acid (1 drop excess), and the colour compared with those of a scale of standards containing 0·5 to 20 ml. of selenious acid solution and 8 ml. of sulphuric acid, and treated in the same manner as the assay.

The selenious acid solution is prepared from 0·0500 g. of selenium by solution in strong nitric acid, evaporation on a water-bath, solution in water, and dilution to 1 litre.

(2) *Fusion method.* The procedure is the same as that given in § VII, *c*, 2, the operations being carried out quantitatively. Sodium peroxide is to be preferred to sodium nitrate or even nitrite; in the case of rich sulphide ores, the peroxide may be diluted with sodium carbonate. A substantial cover of flux should be provided as a safeguard against volatilization loss.

For the determination of selenium in acid-insoluble antimony oxide ore (cervantite),[2] portions of 2·5 g. are fused with sodium peroxide in iron crucibles, the fluid melt being poured on to an iron lid, and disintegrated with water in a 600-ml. beaker. The hot suspension is acidified with strong hydrochloric acid until a clear solution results; this is treated with a liberal excess of 20 per cent. stannous chloride solution at 70° to 80° C. (Treatment of precipitate: § III, *m*, 4.)

(3) *Chlorination method.* The principle of this method has been explained in § III, *k* and § VII, *c*, 1. It may prove a useful alternative for mixtures other than sulphide ores, containing clay, or silicates decomposed by acids, or other constituents exerting an undesirable effect in the acid attack or fusion method.

(*b*) *Materials Rich in Selenium and Tellurium.*—In practice, this work is confined to rich anode slimes and commercial selenium and tellurium. On

[1] W. C. Hughes and H. N. Wilson, *J. Soc. Chem. Ind.*, 1936, **55**, 359T.

[2] W. R. Schoeller, *loc. cit.*

rare occasions, the analyst may be called upon to examine a specimen of hand-picked telluride mineral such as sylvanite; this will be discussed in § IX.

(1) *Rich anode slimes.*[1] The powder (0·5 g.) is heated in a 250-ml. beaker with 10 ml. of concentrated sulphuric acid until decomposed, leaving only a white residue. When cold, the acid is diluted with 40 ml. of water, the silver is precipitated by gradual addition of a slight excess of hydrochloric acid, and the silver chloride coagulated by agitation. The precipitate is filtered off on a small pad of filter-pulp and washed with water containing a few drops of sulphuric acid. The filtrate (100 ml.) is treated with 3 g. of tartaric acid and 80 ml. of strong hydrochloric acid, and the selenium and tellurium are precipitated with sulphur dioxide. The precipitate is collected on an asbestos pad, washed with 5 per cent. hydrochloric acid containing sulphur dioxide, returned to the beaker, and dissolved by digestion with strong hydrochloric acid and potassium chlorate (or bromine). The resultant solution is filtered through asbestos, which is washed with hydrochloric acid (80 per cent. by volume), and the selenium and tellurium are determined in the filtrate as under § III, *n*, 1.

(2) *Commercial selenium.*[2] The powdered material (0·5 g.) is heated in a covered 150-ml. beaker with 10 ml. of water and 15 ml. of concentrated nitric acid. When solution has taken place, the acid is evaporated on the water-bath. The dry residue is dissolved in 10 ml. of hydrochloric acid and 20 ml. of cold water, the insoluble matter filtered off, and washed with dilute hydrochloric acid. The acidity of the filtrate is adjusted with strong hydrochloric acid to 80 per cent. by volume, and the selenium is precipitated at 20° C. with a slow current of sulphur dioxide (2 bubbles per second) during agitation. When the solution smells strongly of the gas the beaker is set aside for half an hour. The solution is then decanted through a porous porcelain crucible, the precipitate washed three times in the beaker with strong hydrochloric acid, and once with hot water, which causes it to turn black. It is collected, washed with hot water, then with alcohol, and determined as usual (§ IV, *a*, 1).

The filtrate is treated with 4 times its volume of water, 3 g. of tartaric acid, 25 ml. of ammonia, saturated with sulphur dioxide, boiled, and digested on a hot-plate for 2 hours. The tellurium precipitate is collected in a porous crucible, washed with hot water and alcohol, dried, and weighed.

(3) *Commercial tellurium.*[3] (*a*) The finely powdered metal (0·5 g.) is dissolved by heating with 10 ml. of strong sulphuric acid until white fumes are evolved. When cold, the acid is diluted with 20 ml. of water, cooled, and treated with 50 ml. of strong hydrochloric acid. Selenium is precipitated at 20° C. by 4 minutes' treatment with sulphur dioxide, and filtered off on a porous porcelain crucible as soon as it has settled. If filtration is unduly delayed, there is a risk of incipient tellurium precipitation. The selenium is determined as usual (§ IV, *a*, 1).

The filtrate containing the tellurium is diluted to 700 ml., heated almost to boiling, and treated with a few grams of hydrazine hydrochloride and a vigorous current of sulphur dioxide until the tellurium settles. It is collected, washed with water and alcohol, dried, and weighed (§ IV, *b*, 1).

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[1] After V. Lenher, in W. W. Scott's *Standard Methods of Chemical Analysis*, 4th edition, New York, 1925, 1, 440*a*.

[2] V. Lenher, *ibid.*, p. 439.

[3] V. Lenher, *ibid.*, p. 440.

($\beta$) *Direct volumetric determination of tellurium.* 0·25 g. of the element is dissolved in 5 ml. of nitric acid (1 : 1), and the solution evaporated to dryness on the water-bath. The residue is dissolved in 15 ml. of strong hydrochloric acid, and the determination carried out as explained in § V, *b*, 1.

§ **IX. Complete Analysis of Ores.**—(*a*) In the complete analysis of *common sulphide ores*, which carry only minute amounts of selenium and tellurium, if any, the operations for the determination of the base metals, sulphur, silicates, etc. are supplemented by a separate determination of the two elements on a more or less considerable quantity (*e.g.* 20 g.) of ore by one of the methods described in § VIII, *a*.

It may be recalled here that comparatively low percentages of the two elements may interfere in other determinations (§ III, *b*), hence the analyst may find it advisable to determine selenium and tellurium first before proceeding with the rest of the analysis.

(*b*) *Rich Telluride or Selenide Minerals.*—The analysis of these minerals must take into account the possible presence of gold, silver, thallium, and all the members of the hydrogen-sulphide group except tin and cadmium.

*First portion: gold, silver, selenium, tellurium, insoluble gangue.* One g. of fine powder is heated in a covered tall 400-ml. beaker (without spout) with 10 ml. of strong sulphuric acid. When cold, the acid is diluted with 10 ml. of water; should any darkening occur, 1 ml. of nitric acid is added and the liquid again heated until the nitric acid is expelled. The solution is diluted to 50 ml., set aside till clear, and filtered.

The insoluble fraction contains gold, lead sulphate, and insoluble gangue. The lead sulphate is extracted with strong ammonium acetate solution, and the residue washed with hot water, ignited, and weighed as gold *plus* gangue. The gold is then dissolved in *aqua regia* and determined as usual.

The filtrate from the insoluble fraction is heated, and precipitated with 2 ml. of hydrochloric acid. The silver chloride is left to settle, collected, washed with water containing a few drops of sulphuric acid, and finally twice with water, and determined gravimetrically.

The filtrate from the silver chloride is treated with 3 g. of tartaric acid, concentrated to 100 ml., diluted with 80 ml. of strong hydrochloric acid, and treated with sulphur dioxide, etc. for the determination of selenium and tellurium as in § VIII, *b*, 1.

*Second portion: lead, bismuth, copper, mercury, arsenic, antimony, iron, thallium.* One g. of powdered ore is dissolved in hot hydrochloric acid, and potassium chlorate added in small portions. When decomposition is complete the solution is gently boiled for the expulsion of chlorine, diluted with 3 to 4 times its volume of water, treated with 3 g. of tartaric acid, and filtered. The residue contains the gangue and silver chloride, which it may be advisable to test for lead chloride.

The filtrate is treated with strong hydrochloric acid to one-third its volume, saturated with sulphur dioxide, and set aside till clear. The precipitate, consisting of gold, selenium, and tellurium, should be tested for bismuth by extraction with nitric acid, filtration from the gold, evaporation of the filtrate till the excess acid is removed, addition of potassium hydroxide in excess, and saturation with hydrogen sulphide. The precipitated bismuth sulphide is collected, washed with dilute potassium sulphide solution, reserved, and added to the main bismuth fraction (*below*).

The filtrate from the gold, etc. is left on a hot-plate until the sulphur dioxide is expelled, and saturated with hydrogen sulphide. The precipitate is collected and extracted with potassium sulphide. The operation results in an insoluble fraction (sulphides of bismuth, lead, and copper), and a filtrate containing mercury, arsenic, and antimony. This latter is boiled with ammonium chloride, mercuric sulphide being precipitated, while arsenic and antimony remain dissolved.

The filtrate from the hydrogen-sulphide precipitate is treated with ammonium chloride and sulphide, giving a precipitate of ferrous and thallous sulphides. This is dissolved in dilute sulphuric acid, the hydrogen sulphide boiled off, and the iron oxidized by boiling with nitric acid and then precipitated with ammonia. The precipitation should be repeated. The thallium in the filtrate is recovered and weighed as chromate (see **XI,** § IV, *a*).

If nickel and cobalt are present, they are precipitated, together with iron, by sodium carbonate (double treatment), thallium passing into the filtrate.

*Third portion: sulphur.* One g. of ore is dissolved in *aqua regia.* The nitric acid is expelled by evaporation, followed by double evaporation with hydrochloric acid. The residue is taken up in dilute hydrochloric acid, and all the heavy metals are precipitated with chemically pure zinc. The metallic sponge is filtered off, the acidity of the filtrate adjusted with dilute ammonia, and the sulphate precipitated with barium chloride.

## XX.—MOLYBDENUM.

§ **I. Minerals.**—There are two minerals of practical importance: molybdenite and wulfenite.

(*a*) *Molybdenite,* the disulphide, is readily identified by its physical properties, as it occurs in grey, soft, flexible scales, which mark paper and are scratched by the finger-nail. It bears a close resemblance to graphite, from which it is distinguished by its lighter colour and streak, but with greater certainty by its behaviour on heating, when it evolves sulphur dioxide and is converted into a yellow powder (the trioxide). H. 1 to 1·5; sp. gr. 4·4 to 4·8. A colloidal mineral of the same composition has been called *jordisite.*

(*b*) *Wulfenite,* $PbMoO_4$, occurs as soft, heavy, lustrous crystals belonging to the tetragonal system. The colour is variable through several shades of yellow, orange, olive-green, almost white, brown or bright red, but usually wax-yellow. It is soluble in hydrochloric or nitric acid. H. 3; sp. gr. 6 to 7.

(*c*) *Molybdite,* or *molybdic ochre,* has been described as molybdenum trioxide, but it usually contains iron and is possibly a hydrated ferric molybdate. It does not occur independently, but accompanies molybdenite, from which it is derived by oxidation. It forms a yellowish powder or incrustations; sometimes it is fibrous or crystalline. Its colour is paler than that of tungstic ochre (*q.v.*); the latter, unlike molybdite, is insoluble in acids.

(*d*) *Powellite* is calcium molybdate, tungsten partly replacing molybdenum: $Ca(Mo,W)O_4$. It is a yellow mineral isomorphous with wulfenite and scheelite, which it sometimes accompanies.

(*e*) Other minerals have been described, *e.g.* *belonosite*, $MgMoO_4$; *pateraite*, impure $CoMoO_4$; *ilsemannite*, a blue oxide, $MoO_2.4MoO_3$ or $Mo_3O_8.nH_2O$; and *achrematite*, $3[3Pb_3(AsO_4)_2.PbCl_2].4Pb_2MoO_5$. Small quantities of molybdenum are sometimes found in iron and copper ores.

§ **II. Properties and Compounds.**—(*a*) The *metal* may be obtained by the decomposition of molybdenite in the electric furnace, by the reduction of the trioxide with aluminium, hydrogen, or carbon, or by the electrolysis of the trioxide in a suitable electrolyte. It is white, hard, and malleable; soluble in nitric or strong sulphuric acid. Sp. gr. 9·01 to 10·32 according to the mechanical treatment; m.p. about 2500° C.

(*b*) *Sulphides.*—The *trisulphide*, $MoS_3$, is slowly precipitated by hydrogen sulphide in acid solution, the latter sometimes acquiring a blue colour. Precipitation is usually incomplete when the gas is passed in the normal manner, since a high concentration of hydrogen sulphide is required to carry the reaction to completion. It is possible to effect complete precipitation either by working under pressure or by acidifying an alkaline thiomolybdate solution and passing in hydrogen sulphide.

The trisulphide is a dark brown powder insoluble in dilute acids, but soluble in alkaline sulphides to a dark red solution containing thiomolybdates ($M^I_2MoS_4$, $M^I_2Mo_2S_7$, and $M^I_2Mo_3S_{10}$), from which it is reprecipitated on acidification. When heated in a current of hydrogen the trisulphide is converted into the *disulphide*, $MoS_2$, which latter is reduced to metal at a higher temperature. On ignition in air both sulphides furnish the trioxide.

(*c*) The *trioxide*, $MoO_3$, is an almost white powder, which becomes transiently yellow when heated. Unlike the corresponding tungsten compound it cannot be ignited without loss at the full heat of the Bunsen flame, as it is appreciably volatile above 500° C. It is soluble in ammonium hydroxide and caustic alkalis. When boiled with potassium iodide and hydrochloric acid it is reduced to the *pentoxide*, $Mo_2O_5$, and a corresponding amount of iodine is set free.

(*d*) *Molybdic acid*, $H_2MoO_4$, separates as a white precipitate when molybdate solutions are acidified; the precipitate is soluble in excess of acid or alkali. The hydrochloric-acid solution, when reduced with zinc, yields an oxide which corresponds approximately to the sesquioxide, $Mo_2O_3$. The yellow crystalline crusts which often deposit from the acid molybdate solution used for the determination of phosphoric acid consist of the monohydrate, $H_2MoO_4.H_2O$.

(*e*) *Ammonium Molybdates.*—The *normal* salt, $(NH_4)_2MoO_4$, is stable only in the presence of excess of ammonia, being decomposed by water into the *heptamolybdate*, $(NH_4)_6Mo_7O_{24}.4H_2O$. The latter forms large colourless crystals, and is the salt sold as " ammonium molybdate."

(*f*) *Lead molybdate*, $PbMoO_4$, precipitated from acetic-acid solution by neutral lead acetate is a cream-coloured crystalline powder, soluble in nitric or hydrochloric, insoluble in dilute acetic, acid. It remains unchanged on ignition.

(*g*) *Mercurous molybdate*, $Hg_2MoO_4$, is precipitated by mercurous nitrate from neutral molybdate solutions. It is white, soluble in nitric acid, and on ignition leaves molybdenum trioxide.

(*h*) *Ammonium phosphomolybdate*, $(NH_4)_3PO_4.12MoO_3.2HNO_3.H_2O$, is a bright yellow crystalline precipitate insoluble in nitric acid, formed when a large excess of ammonium molybdate solution acidified with nitric acid is added to a solution of an orthophosphate.[1]

(*i*) The *molybdenum-oxine complex*, $MoO_2(C_9H_6ON)_2$, is obtained as a compact yellow precipitate when an acetic-acid solution of oxine (8-hydroxyquinoline) is added to a feebly acid alkali molybdate solution containing ammonium acetate. When dried at 130° to 140° C. the precipitate, which has the above composition, is insoluble in acids, even *aqua regia*.

§ **III. Quantitative Separation.**—The analytical chemistry of molybdenum has undergone little change in the past twenty years. A number of electrometric methods have been proposed for the determination of molybdenum in the presence of associated elements in alloy steels. Organic precipitants have found some application, but undoubtedly the gravimetric lead molybdate method is still of most general use for the determination of molybdenum. The separation of molybdenum from tungsten has been critically examined, and conditions worked out.

Molybdenum belongs to the hydrogen-sulphide group; the solubility of its sulphide in alkali-sulphide solution places it in the arsenic-antimony-tin subgroup.

(*a*) *From Iron.*—(1) The following process is more convenient than separation by hydrogen sulphide: An acid solution of molybdic acid and ferric salt is nearly neutralized with sodium hydroxide and poured into hot 8 to 10 per cent. sodium hydroxide solution (40 to 50 ml. for 0·2 g. of iron). The liquid is heated to boiling, the precipitate allowed to settle, collected on a filter, and washed with hot water. If the hydroxide precipitate is large it is best to dissolve and reprecipitate it, or to make the solution and precipitate up to volume in a graduated flask, and after filtration through a dry paper take an aliquot portion of the filtrate. If alkaline earths are present sodium carbonate should be used instead of the hydroxide, and a double precipitation should be performed. The alkaline filtrate is slightly acidified with hydrochloric acid, treated with ammonium acetate, and precipitated with lead acetate (§ IV, *a*).

(2) The solution, neutralized as closely as possible with ammonia without the appearance of a cloudiness, is heated nearly to boiling, and poured slowly during vigorous agitation into 75 ml. of almost boiling 1 : 1 ammonia (sp. gr. 0·94). The precipitated ferric hydroxide is allowed to settle, collected, washed with hot water, dissolved in a small excess of acid, and the precipitation repeated. With more than 0·2 g. of each element present, a third precipitation should be made. It is essential that the

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[1] It is claimed by S. Kitajima (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1931, **16**, 285–327) that at a suitable concentration of ammonium nitrate, molybdenum can be quantitatively precipitated as ammonium phosphomolybdate.

molybdenum solution be poured into the ammonia and that loss of ammonia by boiling be avoided, or there is a danger of occlusion of molybdenum in the precipitate in the form of basic ferric molybdate. In the case of large amounts of iron (0·5 g. and over), method (1) is to be preferred.

(*b*) *From Sulphuric Acid.*—The most accurate method consists in precipitating the molybdenum as lead molybdate. Two cases may be distinguished:

(1) If the molybdenum is to be determined, the precipitation is carried out as in § IV, *a*, 2.

(2) If the determination of sulphuric acid is required (*e.g.* sulphur in molybdenite), the method given under § X, *a*, 3 is employed.

(*c*) *From Arsenic.*—(1) Arsenic may be volatilized as trichloride by distillation with strong hydrochloric acid and a reducing agent.[1]

(2) *From arsenic and phosphorus.* The ice-cold molybdate solution containing arsenic or phosphoric acid, or both, in a volume of not more than 100 ml. per 0·1 g. of the anhydrides, is rendered just acid and treated with an excess of magnesia mixture, followed by strong ammonia added dropwise during vigorous agitation until the solution is alkaline, and then 5 ml. in excess for each 100 ml. of solution.

If elements such as tin, antimony, germanium, and vanadium are also present in solution, tartaric or citric acid should be added prior to the precipitation, and the excess of magnesia mixture should be increased. The precipitate is allowed to stand from twelve to forty-eight hours according to the quantity of arsenic present. If only arsenic is required, 0·5 g. of sodium phosphate ($Na_2HPO_4.12H_2O$), equivalent to about 0·1 g. $P_2O_5$, may be added as a collector. The precipitate is collected, washed with ammonium hydroxide (5 per cent. by volume), dissolved in acid, and the precipitation repeated once or twice more. The molybdenum may be recovered from the combined filtrates as lead molybdate.

(*d*) *From Antimony: Schoeller and Powell's Method.*[2]—The chloride solution, free from nitrates or sulphates, and containing 20 to 25 ml. of strong hydrochloric acid in a bulk of 100 ml., is boiled gently with about 5 g. of pure granulated or thin sheet lead for 20 to 30 minutes. The liquid first assumes a greenish-blue colour, which gradually changes to brown, due to the reduction of the molybdic acid, while the antimony is precipitated in the metallic state. When reduction is complete the liquid is diluted with boiling water and rapidly filtered, the paper being washed with hot water. The filtrate is boiled with a slight excess of nitric acid to re-oxidize the molybdenum, partly neutralized with ammonia, heated to boiling, and precipitated with 50 ml. of 25 per cent. ammonium acetate solution; the lead molybdate is ignited and weighed. The precipitated antimony is dissolved, together with the lead, in 10 ml. of strong nitric acid and 40 ml. of 20 per cent. tartaric acid solution, the lead removed as sulphate, and the antimony in the filtrate precipitated with hydrogen sulphide.

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[1] C. Friedheim and P. Michaelis (*Ber.*, 1895, **28**, 1414) recommend methyl alcohol; C. Friedheim, O. Decker, and E. Diem (*Zeitsch. anal. Chem.*, 1905, **44**, 665) use potassium iodide.

[2] Originally published in the first edition of this work.

(*e*) *From Vanadium.*—The solution containing molybdenum and vanadium is treated with tartaric acid and excess of ammonia, saturated with hydrogen sulphide, just acidified with dilute sulphuric acid, and hydrogen sulphide passed for a further 15 minutes. The precipitate of molybdenum sulphide is collected, washed with 1 per cent. sulphuric acid containing hydrogen sulphide, dissolved in alkali with addition of tartaric acid, and reprecipitated.[1] The vanadium may be recovered from solution with cupferron or tannin (*cf.* **XVII,** § IV).

(*f*) *From Tin.*—(1) If the tin is present in the ore as cassiterite, it will remain in the insoluble portion after the decomposition of the ore by acids.

(2)[2] The solution of molybdic acid and stannic chloride, containing not more than 0·3 g. of the metals (Mo + Sn), 10 ml. of strong hydrochloric acid, and 3 ml. of nitric acid, is treated with a solution of ferric iron equal in weight to the tin presumed to be present. It is diluted to about 100 ml., heated to incipient boiling, and poured during vigorous agitation into 100 ml. of dilute ammonia (20 ml. of ammonia sp. gr. 0·88 and 80 ml. of water) previously heated almost to boiling, the beaker being rinsed with 2 per cent. ammonium nitrate solution, and boiled for half a minute. The precipitate is allowed to settle, collected on a close-textured filter, washed with hot 2 per cent. ammonium nitrate solution, returned to the beaker by means of a jet of water, and dissolved in 10 ml. of strong hydrochloric acid (total volume about 50 to 60 ml.). The solution is heated until the precipitate has dissolved, diluted to 100 ml., and the precipitation repeated. The precipitate is collected on the same filter and washed as before. The combined filtrates are evaporated to 200 ml. and the molybdenum precipitated as lead molybdate (§ IV, *a*). The tin is determined in the ammonia precipitate by the usual methods.

(3) Quadrivalent tin may be completely volatilized by dry hydrochloric acid gas passed through a sulphuric-acid solution heated to about 200° C.

(*g*) *From Small Amounts of Phosphorus, Arsenic, Antimony, and Vanadium.*—Precipitation with ammonia as under *a*, 2, *above*, affords a complete separation of molybdenum from the above elements, provided a sufficiently large excess of ferric iron is present. If necessary, iron is added to ensure at least a tenfold excess over that of the elements to be removed.[3]

(*h*) *From Lead.*—(1) Sulphuric acid is added to the solution, which is then evaporated until copious fumes of sulphuric acid are evolved. The liquid is cooled, diluted with nine times its volume of water, boiled until the molybdic acid dissolves, and allowed to stand overnight. The lead sulphate is collected and washed with 5 per cent. by volume sulphuric acid.

(2) Lead may be precipitated from alkaline solution with hydrogen sulphide.

(*i*) *From Copper.*—(1) Copper is not quantitatively precipitated from alkaline sulphide solution in the presence of a large excess of molybdenum, but may be deposited electrolytically from solutions containing sulphuric and nitric acids.[1]

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[1] A. E. Stoppel, C. F. Sidener, and P. H. M. P. Brinton, *Chem. News*, 1925, **130**, 353–5.

[2] D. A. Lambie and W. R. Schoeller, *Analyst*, 1940, **65**, 281.

[3] Hillebrand and Lundell, *op. cit.*, add 0·1 g. of iron per 0·01 g. of vanadium (p. 355); 0·1 to 0·2 g. of ferric salt per 0·01 g. of arsenic (p. 213); and 0·1 g. of iron per 0·01 g. of antimony (p. 227).

(2) The solution containing copper and molybdenum, and 6 to 7 ml. of strong sulphuric acid in a volume of 200 to 300 ml., is boiled and treated with N. sodium thiosulphate solution (§ IX, *b*).

(*j*) *From Tungsten.*—(1) Molybdenum sulphide is precipitated free from tungsten when the tartrate solution is treated with hydrogen sulphide.[2] The solution of molybdate and tungstate is treated with 10 to 15 g. of tartaric acid and rendered alkaline with caustic soda. It may now be acidified with 1 : 1 sulphuric acid (according to Werz it is necessary to make alkaline after addition of the tartaric acid to form a stable tungsten-tartaric acid complex),[3] heated to 80° C., and the molybdenum precipitated with a rapid current of hydrogen sulphide; if more than 30 mg. of molybdenum is present, precipitation may not be complete.[3] Alternatively, the cold alkaline solution is saturated with hydrogen sulphide, acidified with 1 : 1 sulphuric acid, and hydrogen sulphide passed for a further quarter of an hour; the molybdenum is completely precipitated.[4] However produced, the precipitate is collected and washed with 1 per cent. sulphuric acid containing hydrogen sulphide. For the subsequent treatment of the precipitate, see §§ IV, *c* and *d*, V, VI, and VIII, *a*. The filtrate is evaporated in a 1-litre beaker with 20 ml. of 1 : 1 sulphuric acid, and the tartaric acid destroyed with nitric acid. The tungsten is recovered as under **XXI**, § IV, *c*.

(2) The solution of sodium molybdate and tungstate (10 to 15 ml.) is treated with 10 ml. of 50 per cent. ammonium formate, 10 ml. of 30 per cent. tartaric acid solution, and 100 ml. of water saturated at 0° C. with hydrogen sulphide, followed by 10 ml. of 2M. formic acid, and the liquid is heated at 60° C. for one hour. A little filter-pulp is stirred in, 10 ml. of 24M. formic acid added, and the solution heated for a further 30 minutes on the water-bath. The precipitate of molybdenum sulphide is collected and washed with a solution of 5 ml. of 50 per cent. ammonium formate and 5 ml. of 24M. formic acid per 100 ml. of water.[5] The tungsten is recovered from the filtrate after elimination of the tartaric acid.[6]

§ **IV. Gravimetric Determination.**—Molybdenum may be weighed as disulphide or trioxide, but preferably as lead molybdate or the oxine complex.

(*a*) *Determination as Lead Molybdate.*—This is the most accurate and expeditious method, the advantages of which, summarized by Bonardi,[7] are as follows: Lead molybdate is stable at high temperatures and, unlike lead sulphate, is not reduced by contact with glowing carbon; hence no special precautions need be exercised during its ignition. The conditions of precipitation, acidity, and concentration of salts may be varied within wide limits, although too great an excess of lead acetate is to be avoided, especially in the presence of sulphates. Finally, the molybdenum is weighed in combination with a metal of high atomic weight.

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[1] W. Hoepfner and O. Binder, *Chem. Zeit.*, 1918, **42**, 315.

[2] H. Rose, *Handbuch der analytischen Chemie*, 1871, p. 358.

[3] W. Werz, *Zeitsch. anal. Chem.*, 1935, **100**, 241–257.

[4] A. H. Low, *Technical Methods of Ore Analysis*, 9th edition, 1922, p. 163.

[5] H. Yagoda and H. A. Fales, *J. Amer. Chem. Soc.*, 1936, **58**, 1494–1501.

[6] Yagoda and Fales precipitate the tartaric acid as ammonium bitartrate by addition of 50 ml. of 95 per cent. alcohol to the filtrate concentrated to 25 ml. This is collected, washed with 50 per cent. alcohol, charred with 0·5 g. of sodium carbonate, and the mass leached with water and filtered. The tungsten is precipitated in the combined filtrates by means of nitric acid and cinchonine. We prefer to destroy the tartaric acid with nitric acid and precipitate tungsten with tannin and cinchonine as under (1), *above*.

[7] J. P. Bonardi, *Bull.* **212**, *U.S. Bur. Mines*, p. 108.

(1) The alkaline molybdate solution, containing not more than 0·3 g. of molybdenum, is acidified with 2 ml. of acetic acid, treated with 5 g. of ammonium chloride per 100 ml. of liquid, and precipitated whilst boiling with a 4 per cent. lead acetate solution, which is added dropwise with constant stirring. The beaker is kept on a hot-plate until the precipitate has settled; this is collected on a close-textured filter having a pulp pad in the apex, and washed with hot 2 per cent. ammonium acetate solution by decantation at first, then on the filter until the washings fail to give a coloration with sodium sulphide solution. The small quantity of precipitate which adheres to the beaker and stirring rod is most readily removed by means of a little filter-pulp. The moist filter is folded so that the portion containing the precipitate lies uppermost in the crucible, which is then heated on an asbestos gauze until the paper is charred; the carbon is burned off at a low temperature, and the precipitate heated for a short time to dull redness, cooled, and weighed.

(2) In the majority of cases the solution in which the molybdenum is to be determined contains also sulphate, derived from the sulphur with which the metal was combined, or sulphuric acid used in previous separations. Its presence may lead to high results, although Schoeller and Powell,[1] by using a large excess of ammonium acetate and adding the lead acetate dropwise, and Bonardi and Barrett,[2] by limiting the amount of lead acetate, secure a complete separation in a single precipitation.

The molybdate solution (volume about 350 ml.) is rendered just acid to methyl orange with 1 : 1 hydrochloric acid; 5 ml. of glacial acetic acid and 25 ml. of 50 per cent. ammonium acetate solution are added. Lead acetate solution (40 g. of the crystallized salt and 10 ml. of acetic acid per litre) is added dropwise from a burette to the boiling molybdate solution, which is stirred continuously. The addition is continued until a test-drop taken from the solution gives no colour change with a drop of freshly prepared tannin solution (0·1 g. in 20 ml. of water); 2 to 5 ml. excess of the lead solution is then added, and the beaker maintained at boiling-point for fifteen minutes or until the precipitate has become granular and settles well. The further treatment of the precipitate is as described *above*.

Should an excessive amount of sulphuric acid be present, it is advisable to dissolve and reprecipitate the lead molybdate: the unwashed precipitate is dissolved in 1 : 1 hydrochloric acid, which is diluted to 200 ml. with hot water, the boiling solution treated with 1 : 1 ammonia until a slight turbidity forms, this being cleared by cautious addition of 1 : 1 hydrochloric acid, and finally 25 ml. of 50 per cent. ammonium acetate solution is added. The solution is boiled until the precipitate becomes granular, and the determination completed as before.

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[1] First edition of this work, p. 164.

[2] J. P. Bonardi and E. P. Barrett, *Tech. Paper* 230, *U.S. Bur. Mines*, 1920.

When the amount of molybdenum is very small the solution should be heated for several hours and allowed to stand overnight for the deposition of the lead molybdate.

The following elements must be removed prior to the precipitation, since they give a precipitate under the conditions of the method: lead, barium, calcium, strontium, silicon, arsenic, antimony, phosphorus, chromium, aluminium, iron, vanadium, and tungsten.

(*b*) *Determination as Oxine Complex.*[1]—The solution of alkali molybdate is diluted to 50 to 100 ml. after being neutralized to methyl red, acidified with two drops of 5 per cent. by volume sulphuric acid, and 5 ml. of 15 per cent. ammonium acetate solution added. The solution is boiled and treated during agitation with a 5 per cent. solution of 8-hydroxyquinoline in 25 per cent. acetic acid, until present in slight excess; it is then boiled gently for a further two or three minutes. The precipitate is collected on a Gooch or sintered glass crucible, washed with hot water, dried to constant weight at 130° to 140° C., and weighed as $MoO_2(C_9H_6ON)_2$. (Mo factor: 0·2305.)

This method provides a separation from rhenium (*q.v.*), but the molybdate solution should be free from metals other than the alkalis. It is not possible to apply the volumetric method to the dried precipitate, since it is insoluble both in acids and in alkalis.

(*c*) *Determination as Disulphide.*—The sulphate or chloride solution, free from other metals of the hydrogen-sulphide group, is made alkaline with ammonia, saturated with hydrogen sulphide, and rendered acid with 1 : 1 sulphuric acid (2 per cent. by volume excess). Hydrogen sulphide is then passed for a further fifteen minutes to complete the precipitation of the molybdenum sulphide.[2] Molybdenum is also completely precipitated if a rapid stream of hydrogen sulphide is passed through the sulphuric-acid solution heated to 80° C., provided not more than 30 mg. is present.[3] With larger amounts of molybdenum a milligram or so may escape precipitation, being reduced to compounds of a lower valency. In this case, the precipitate is collected and washed, the filtrate freed from hydrogen sulphide by boiling, and then treated with an oxidizing agent such as ammonium persulphate to re-oxidize the molybdenum, which is then precipitated as sulphide.

In either case the precipitate is collected and washed at first with 1 per cent. sulphuric acid containing hydrogen sulphide, then with 50 per cent. alcohol. The filter and precipitate are dried and separated as completely as possible, the former being burned at a very low temperature in a tared Rose crucible. The bulk of the precipitate, together with half its weight of sulphur, is transferred to the crucible, which is then ignited at a dull red heat in a stream of hydrogen for about fifteen minutes.[1] If the temperature is too high or the ignition protracted the disulphide begins to decompose into its elements; in fact the whole of it can be reduced by the use of a blast-lamp.[2] This process requires considerable care and practice, and has no advantage over the preceding methods.

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[1] W. Geilmann and F. Weibke, *Zeitsch. anorg. Chem.*, 1931, **199**, 347.

[2] A. H. Low, *op. cit.*, p. 163.

[3] W. Werz, *loc. cit.* According to M. Straumanis and B. Ogrims (*Zeitsch. anal. Chem.*, 1939, **117**, 30) formation of molybdenum blue is avoided if the concentration of $MoO_3$ is not greater than 30 mg. per 100 ml. and if the acid (hydrochloric, sulphuric, or nitric) is 0·02 to 0·1N., a rapid current of hydrogen sulphide being passed through the cold solution for 5 to 10 minutes, and continued whilst the solution is boiled for 10 minutes. The solution is allowed to cool and stand for an hour before filtration.

(*d*) *Determination as Trioxide.*—(1) Instead of being treated as described *above*, the precipitate may be oxidized to trioxide. This operation must be conducted with care, as the temperature may rise to the point of incipient volatilization of the trioxide. According to Brinton and Stoppel,[3] sublimation of the oxide starts at 500° C.; between 500° and 600° C. the loss is not greater than 0·1 mg. per hour in ordinary operations. Various schemes have been suggested to avoid loss from this cause. Thus the wet filter and precipitate are placed in a tared crucible and dried at 100° C. The covered crucible is then gently heated until volatile hydrocarbons have been driven off. The lid is removed and the tarry matter around the inner sides burned off at a very low temperature. The precipitate is then mixed with mercuric-oxide suspension, evaporated to dryness, and heated for the expulsion of the mercury.[4]

According to Binder,[5] the sulphide should be ignited, the residue evaporated with nitric acid, dissolved in ammonia, reprecipitated with nitric acid, evaporated to dryness, and re-ignited; a correction should be made for any matter in the residue insoluble in ammonia. If any insoluble residue is obtained, we consider it more accurate once more to evaporate the ammoniacal filtrate with nitric acid and gently ignite the residue to pure $MoO_3$.

Hillebrand and Lundell[6] confine this method (which is still considered the standard procedure in Germany[7]) to the determination of small amounts (2 to 10 mg.) of molybdenum, a practice with which we fully agree.

(2) The trioxide may also be obtained by ignition of mercurous molybdate at low temperature. Mercurous nitrate solution is added in slight excess to the molybdate solution, which has been rendered feebly alkaline with sodium carbonate, and the solution is boiled. The precipitate is collected, washed with water containing 1 ml. of saturated mercurous nitrate solution per litre, dried, and separated from the filter. Any precipitate remaining on the filter is dissolved in nitric acid, the solution collected in a tared crucible, and evaporated to dryness. The rest of the precipitate is added and the crucible heated gently until the mercury is expelled.

The molybdate solution must be free from tungstate, arsenate, chromate, vanadate, phosphate, sulphate, silicate, and chloride. It is difficult to remove all alkali salts from the precipitate by washing, and for this reason the method is prone to give high results even when applied to pure alkali molybdate solutions.

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[1] *Bull.* **212**, *U.S. Bur. Mines*, p. 84.

[2] O. Freiherr v. d. Pfordten, *Ber.*, 1884, **17**, 734.

[3] P. H. M. P. Brinton and A. E. Stoppel, *J. Amer. Chem. Soc.*, 1924, **46**, 2454.

[4] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 8th edition, 1935, **2**, 275.

[5] O. Binder, *Chem. Zeit.*, 1918, **42**, 255.

[6] *Op. cit.*, p. 255.

[7] *Ausgew. Methoden*, p. 399.

§ **V. Volumetric Determination.**—The methods for the volumetric estimation of molybdenum present no great advantage over the gravimetric determination as lead molybdate, except where a number of assays are regularly made. Methods (*c*) and (*d*) are not well adapted for ore analysis, but, while the permanganate method gives good results in practised hands, a gravimetric process is advisable where only an occasional determination is required.

(*a*) *Permanganate Titration.*—The sulphate solution, containing not more than 0·3 g. of molybdenum and 10 per cent. by volume of sulphuric acid, and free from other metals which have more than one stage of oxidation, is treated with potassium permanganate until pink. It is then passed through a Jones reductor, the reduced solution being collected in 30 ml. of ferric sulphate solution [1]; 5 ml. of syrupy phosphoric acid is added, and the liquid titrated with decinormal potassium permanganate solution (1 ml. ≡ 3·2 mg. Mo) standardized against sodium oxalate. The molybdenum is reduced to the $Mo^{III}$ stage, and re-oxidized by the permanganate to the $Mo^{VI}$ stage.

(*b*) *Precipitation Method.*—The molybdate solution is acidified with acetic acid, heated to boiling, and titrated with lead acetate solution (20 g. per litre: 1 ml. ≡ approx. 5 mg. Mo) until a drop of the solution fails to give a yellow tint with a drop of freshly prepared 0·5 per cent. tannin solution on a spot plate. This titration is the converse of Alexander's volumetric lead assay. The lead solution is standardized against pure molybdenum trioxide, which is dissolved in caustic alkali, and the solution treated in the same manner as the assay.

In recent years, attempts have been made to replace the tannin by internal indicators of the adsorption type (alizarin red, eosin A, erythrosin), but whilst satisfactory with pure solutions, they fail to give accurate results in the presence of salts unavoidably introduced in the course of an analysis.[2]

This method will not give accurate results with low-grade ores, owing to the slow formation of lead molybdate in solutions containing large quantities of alkali salts.

(*c*) *Iodimetric Method.*[3]—Molybdenum trioxide or a molybdate boiled with potassium iodide and hydrochloric acid is reduced as follows:

$$2MoO_3 + 2HI = Mo_2O_5 + I_2 + H_2O.$$

The determination is carried out in a small distillation flask in a current of carbon dioxide, and the liberated iodine titrated as usual. This process is used for the determination of molybdic acid in complex compounds such as silico- and phosphomolybdates.

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[1] A solution containing 2 g. of iron and 8 ml. of sulphuric acid per 100 ml., prepared by dissolving iron in *aqua regia*, evaporating the solution to fumes with sulphuric acid, and diluting to the required volume (G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1923, **45**, 2621).

[2] C. Rajchinschtein and N. Korobov, *J. Gen. Chem. Russ.*, 1933, **3**, 531; A. C. Rice and L. A. Yerkes, *U.S. Bur. Mines, Rept. Invest.*, 1937, **3328**, 37; C. Candea and I. G. Murgulescu, *Ann. Chim. Analyt.*, 1936, **18**, 33.

[3] C. Friedheim and H. Euler, *Ber.*, 1895, **28**, 2066; F. Hundeshagen, *Zeitsch. anal. Chem.*, 1889, **28**, 144, 171; F. A. Gooch and J. T. Norton, *Amer. J. Sci.* (4), 1898, **6**, 108.

(*d*) *Acidimetric Method.*—Molybdenum trioxide is dissolved in 0·5N. sodium hydroxide, the excess of which is titrated back with 0·5N. acid, phenolphthalein being used as indicator:

$$MoO_3 + 2NaOH = Na_2MoO_4 + H_2O.$$

1 ml. of 0·5N. NaOH ≡ 36 mg. $MoO_3$.

§ **VI. Colorimetric Determination.**—When less than a milligram of molybdenum has to be determined a colorimetric process should be employed, that which utilizes the colour produced by addition of a thiocyanate and stannous chloride to the molybdate solution being the most satisfactory. This method has been critically studied by Hurd and Allen,[1] who find that the colour is most stable in the presence of 5 per cent. of hydrogen chloride and not less than 0·6 per cent. of potassium thiocyanate; it is not sensitive to fluctuations in the stannous chloride concentration.

The molybdenum trioxide is dissolved in ammonia (1 ml.), and the solution evaporated just to dryness. The residue is taken up with 15 ml. of hydrochloric acid (10 per cent. by weight of HCl), and transferred to a comparison cylinder with a little water. A scale of standards is set up with measured quantities of an ammonium molybdate solution standardized by the lead molybdate method, the same amount of acid being added. To each tube are now added 10 ml. of 5 per cent. potassium thiocyanate solution and 10 ml. of a stannous chloride solution (5 g. $SnCl_2.2H_2O$ and 10 g. HCl per 100 ml.), and the solutions diluted to 50 ml. with water and mixed. The colours should be compared without delay. Silicon, iron, aluminium, titanium, thorium, niobium, tantalum, manganese, calcium, phosphorus, and arsenic do not interfere.

The coloured compound is more stable in non-aqueous media, and is readily extracted by means of a number of organic solvents, but ether is to be preferred. Ethyl ether is shaken with one-tenth of its volume of thiocyanate and stannous chloride solutions the same day as it is required. The molybdate solution is treated with the reagents as *above* in a separator, and, after standing for half a minute, extracted with 50 ml. of the ether. After separation, the ethereal layer is transferred to a comparison tube and the colour compared with standards similarly treated. If these solutions are protected against evaporation the colour will be stable for a day. When very small amounts of molybdenum are to be estimated, the volume of ether used in the extraction may be suitably reduced and the comparison made in small stoppered tubes. In addition to the above elements, copper, nickel, cobalt, chromium, vanadium, and uranium do not interfere with this process; tungsten in sufficient quantity and rhenium interfere.

§ **VII. Detection in Ores.**—Molybdenum minerals fused with alkali carbonate and nitrate give a melt containing molybdate, which is identified by the following reactions:

(*a*) The solution, strongly acidified with nitric acid, gives with one drop of a dilute sodium phosphate solution in the presence of ammonium nitrate a bright yellow crystalline precipitate. Stirring and warming favour the precipitation.

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[1] L. C. Hurd and H. O. Allen, *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 396.

(*b*) Metallic zinc reduces the solution acidified with hydrochloric or sulphuric acid, with formation of coloured compounds. If the quantity of molybdenum predominates over that of the added acid the liquid is coloured deep blue; in the presence of an excess of acid, however, it becomes first reddish-yellow and then greenish-blue. Hence, in applying the test, it is advisable to add but little acid. Other elements which give coloured solutions or precipitates under the same conditions are tungsten, niobium, vanadium, and titanium (*qq.v.* : **XXI,** § VII, *a*, 2; **XVIII,** § VI, *b*, 2; **XVII,** § VII, *d*; and **XIII,** § VII, *a*, 2).

(*c*) A most sensitive and characteristic test consists in treating the filtered solution of the melt with potassium or ammonium thiocyanate, acidifying with hydrochloric acid, and adding a piece of zinc. In the presence of molybdenum a red colour develops (this must not be confused with the colour due to ferric iron, which would be bleached by reduction by the zinc and acid). The reaction is rendered more sensitive by agitation of the solution with ether, which extracts the coloured compound.

A variation of this reaction by which 0·001 mg. of molybdenum in a drop (0·02 ml.) can be detected in the presence of titanium, uranium, tungsten, or vanadium, is carried out as follows[1]: A drop of the solution under test acidified with hydrochloric acid is placed on a piece of filter-paper, followed by a drop each of hydrochloric acid and potassium thiocyanate solution. On addition of a drop of stannous chloride the red colour due to ferric iron disappears and a crimson colour due to molybdenum develops.

(*d*) Tannin produces a deep orange coloration in the solution acidified with acetic acid.

(*e*) If a small quantity of the powdered molybdenum mineral is heated with a drop of strong sulphuric acid in a porcelain crucible until the acid is nearly expelled, a deep blue colour develops as the crucible cools; this may be accelerated if the test is breathed upon or a trace of alcohol added.

(*f*) Molybdic acid imparts a greenish colour to the Bunsen flame.

(*g*) Potassium ethylxanthate gives with a mineral-acid solution of a molybdate a plum-red colour which can be extracted with organic solvents, preferably a mixture of 65 per cent. ethyl ether and 35 per cent. light petroleum. It is claimed that this reaction will show the presence of as little as 0·0006 mg. of molybdenum per ml.[2]

(*h*) Molybdenum may be detected in steel without complete solution of the sample by the following procedure[3]: Two or three drops of 50 per cent. nitric acid are placed on a clean surface of the steel, followed at two-minute intervals by 1 or 2 drops of bromine in aqueous potassium bromide, and 20 per cent. sulphuric acid. The reagents are removed by filter-paper, and a drop of 3 per cent. potassium ethlyxanthate solution is placed on the spot on the filter-paper, followed by a drop of 10 per cent. stannous chloride solution. If molybdenum is present a red stain appears. Chromium, nickel, tungsten, and vanadium do not interfere.

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[1] N. A. Tananaev and G. A. Pantschenko, *Ukraine Chem. J.*, 1929, **4**, 121.

[2] J. Koppel, *Chem. Zeit.*, 1919, **43**, 777.

[3] M. E. Petrov, *Zavod. Lab.*, 1936, **5**, 1380.

**§ VIII. Determination in Ores and Alloys.**—(*a*) *Wulfenite.*[1]—One g. of the ore is heated with 15 ml. of strong nitric and 7 ml. of strong sulphuric acid until decomposition has been effected; the liquid is then evaporated until copious fumes of sulphur trioxide are evolved. When cold, about 40 ml. of water is added, and the liquid boiled until the molybdic acid is dissolved, cooled, and filtered, the residue being washed with cold 5 per cent. sulphuric acid.

The residue consists chiefly of lead sulphate, but may contain a little molybdenum, especially if the ore contains tungsten also. It should be extracted with hot ammonium acetate solution, the insoluble from this treatment being collected, ignited gently in a platinum crucible, treated with a few drops of 1 : 1 sulphuric acid and a few ml. of hydrofluoric acid, and evaporated to dryness. If more than a trace of residue remains, it should be fused with a little potassium bisulphate, the melt leached with water, and the solution filtered and added to the bulk.

To the solution containing all the molybdenum is added a ferric alum solution to provide a tenfold excess of iron over the arsenic present in the ore (0·3 to 0·4 g. is usually ample). The acid solution nearly neutralized with ammonia is heated to incipient boiling, and poured with vigorous stirring into 75 ml. of almost boiling 1 : 1 ammonia (sp. gr. 0·94). The ferric hydroxide precipitate is collected, washed with hot water, dissolved in a slight excess of hydrochloric acid, and the precipitation and filtration are repeated; three precipitations are required for large amounts of iron and molybdenum (*cf.* § III, *a*, 2). To the combined filtrates are added 5 g. of tartaric acid and 8 ml. of ammonia (sp. gr. 0·88); the resultant cold solution is saturated with hydrogen sulphide, cautiously acidified with 1 : 1 sulphuric acid, and treated with a rapid stream of the gas for a further fifteen minutes. This treatment should yield a flocculent sulphide precipitate, which settles quickly to leave a colourless solution. The precipitate is collected on a filter and washed with cold 1 per cent. sulphuric acid containing hydrogen sulphide. The precipitate is not readily soluble in acids, but the following treatment has been found satisfactory: The filter containing the sulphides is spread on the side of the beaker and the precipitate rinsed off with a jet of water; a mixture of 10 ml. of strong nitric acid and 10 ml. of saturated bromine water is heated and poured over the paper, which is then rinsed thoroughly with hot water and discarded. The precipitate is dissolved by heating (solution may be expedited by addition of potassium chlorate), the solution boiled until free from bromine, and filtered from the sulphur globules if necessary.

The determination may now be finished by the gravimetric lead molybdate method (§ IV, *a*) or, after evaporation with sulphuric acid to obtain a sulphate solution, by permanganate titration (§ V, *a*). Alternatively, if copper is known to be absent the molybdenum may be precipitated with 8-hydroxyquinoline (§ IV, *b*).

(*b*) *Molybdenite.*—From 0·5 to 5 g. of the finely crushed ore (according to the expected molybdenum content) is treated with 10 to 35 ml. of strong nitric acid and 7 to 10 ml. of strong sulphuric acid, and heated until the molybdenite is decomposed. The solution is evaporated until sulphuric fumes are freely evolved, cooled, diluted with 50 ml. of water, and boiled until the molybdic acid is dissolved. Ferric alum is added and the determination continued as under (*a*), *above.*

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[1] After Electro-Metallurgical Co. and Ledoux & Co., *U.S. Bureau of Mines, Bull.* **212**, p. 122.

(*c*) *Ferromolybdenum.*—A suitable quantity, containing not more than 0·3 g. of molybdenum, is dissolved in *aqua regia* and treated as under (*a*), *above.*

(*d*) *Steel.*[1]—One to two g. of drillings are dissolved in 20 ml. of strong hydrochloric acid and 30 ml. of water, and the solution is oxidized with 15 to 30 ml. of 5 per cent. potassium chlorate solution. After the chlorine has been boiled off, 30 to 60 ml. of 30 per cent. tartaric acid is added, followed by an excess of hot 20 per cent. caustic soda solution. The solution is re-acidified with 1 : 1 sulphuric acid (the colour, at first brown, becomes green on acidification), filtered, and diluted to 300 ml. It is then heated to 80° C. and a rapid stream of hydrogen sulphide passed in. To ensure complete precipitation of molybdenum sulphide under these conditions not more than 0·03 g. of molybdenum should be present. The analysis may be completed by the gravimetric lead molybdate method (§ IV, *a*).

(*e*) *Rapid Method for Molybdenite.*—The following method may be used for assaying substantially pure molybdenite concentrates in technical work: 0·5 to 2 g. is attacked with *aqua regia*, and the solution evaporated to dryness. The residue is digested with dilute caustic soda solution, and the solution acidified with dilute hydrochloric acid and poured almost boiling into hot 10 per cent. caustic soda solution. After being heated for ten minutes, the precipitate is filtered off and washed with hot water. The filtrate is treated for gravimetric or volumetric determination of molybdenum as under § IV, *a*, or § V, *b*.

**§ IX. Determination of Impurities in Ores and Ferromolybdenum.**—(*a*) *Lead* is determined by evaporation of the ore with nitric and sulphuric acids as in § VIII, *a* and *b*, extraction of the lead sulphate with ammonium acetate, and precipitation as lead molybdate.

(*b*) *Copper.*—(1) *In ores.*[2] One g. of ore is heated with 25 ml. of nitric and 6 to 7 ml. of sulphuric acid, and the resulting solution is evaporated until copious fumes are evolved. After being diluted with 100 ml. of water, the liquid is boiled and filtered, and the filtrate diluted to 200 to 300 ml. Normal sodium thiosulphate solution is added from a burette to the boiling liquid until the deep blue solution shows a turbidity due to the separation of sulphur, and the boiling is continued for a short time. The precipitate is mixed with a little filter-pulp, collected on a filter, and washed with water containing sulphurous acid until the washings are colourless. The filter-paper is gently incinerated and the residue dissolved in nitric acid; the copper is determined colorimetrically or volumetrically in the usual manner.

(2) One g. is dissolved in *aqua regia*, the nitric acid expelled by evaporation with hydrochloric acid as usual, and the molybdenum, etc. precipitated with hydrogen sulphide. The sulphide precipitate is dissolved in nitric acid, and the determination completed as under (1).

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[1] W. Werz, *Zeitsch. anal. Chem.*, 1935, **100**, 241–257.

[2] M. G. Raeder, *Tidssk. Kemi Bergvaesen*, 1928, **8**, 91–93.

(*c*) *Arsenic.*—One g. is decomposed with 10 ml. of nitric and 10 ml. of hydrochloric acids, and the solution evaporated to dryness. After repeated evaporation with a further 10 ml. of hydrochloric acid, the residue is digested and transferred with strong hydrochloric acid to a 500-ml. distillation flask (final volume about 150 ml.), 5 g. of cuprous chloride is added, and the arsenic trichloride distilled into ice-cold water. The arsenic in the distillate may be titrated with iodine in the usual manner, but we prefer to precipitate it with hydrogen sulphide, dissolve the precipitate in strong sulphuric acid, and then titrate with iodine in bicarbonate solution.

(*d*) *Bismuth*, *arsenic*, *antimony*, *and tin* are retained quantitatively in the ferric hydroxide precipitate obtained in the determination of the molybdenum (§ VIII, *a*). If necessary a larger quantity of ore may be taken, and the ammonia precipitate analysed for the above metals by the usual methods.

(*e*) *Calcium carbonate* is determined by treatment of the ore with acetic acid, the filtered solution being precipitated with ammonium oxalate.

(*f*) *Tungsten.*— One g. of the finely ground material is heated with 25 ml. of strong hydrochloric acid in a covered 250-ml. beaker for an hour. The cover is removed and the liquid evaporated to about 5 ml., 20 ml. of strong nitric acid is added, and the covered beaker again heated until decomposition is complete. After renewed evaporation to about 5 ml., the mass is taken up with 50 ml. of hot water, and the solution treated with 5 ml. of 5 per cent. cinchonine solution [1] and set aside overnight.

The precipitate containing the tungstic acid is collected, washed with dilute cinchonine solution,[2] and finally once with water to displace most of the cinchonine. It is then returned to the beaker by means of a jet of water and dissolved by heating with 5 ml. of strong ammonia; the solution is filtered through the same filter, which is washed with hot water. Residue and filter are ignited in a platinum crucible, treated with hydrofluoric and sulphuric acids, and the fixed residue fused with sodium carbonate. The melt is dissolved in water, and the solution added to the ammoniacal filtrate containing the bulk of the tungstic acid.

In the case of wulfenite ores, the residue from the acid attack will contain lead chloride in addition to the tungstic and molybdic acids; it should be returned to the beaker and digested with warm saturated ammonium carbonate solution. The lead carbonate residue is filtered off, washed with dilute ammonium carbonate solution (filtrate: $F^1$), dissolved in dilute nitric acid, the solution filtered, the residue washed with 5 per cent. by volume nitric acid, and the filtrate discarded. Filter and residue are ignited and treated with hydrofluoric and sulphuric acids as *above*, the residue is fused with sodium carbonate, and the solution of the melt added to $F^1$.

The alkaline tungstate solution obtained as *above* is freed from molybdenum, and the tungsten determined, as in § III, *j*.

(*g*) *Lead*, *Aluminium*, *Chromium*, *and Vanadium in Ferromolybdenum.*— One g. is dissolved in *aqua regia* and the iron precipitated with ammonium hydroxide; the ferric hydroxide, containing the above elements and some molybdenum, is collected, washed, and dissolved in acid, and the molybdenum and lead are precipitated with hydrogen sulphide. The iron in the filtrate is removed as sulphide from ammoniacal tartrate solution. The filtrate, after being boiled for the removal of ammonium sulphide, is treated with tannin and ammonium acetate to recover the chromium, aluminium, and vanadium, which are separated and determined as under **XVII,** § III, *h* and *j*.

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[1] Fifty g. of the alkaloid dissolved in 500 ml. of 1 : 1 hydrochloric acid, diluted to 1 litre with water, and filtered.

[2] Fifteen ml. of strong hydrochloric acid and 60 ml. of the above cinchonine solution diluted to 1 litre with water.

(*h*) *Silicon and Sulphur in Ferromolybdenum.*—One g. is dissolved in *aqua regia*; after evaporation to dryness on the water-bath and another evaporation with hydrochloric acid, the dry mass is digested with hydrochloric acid. The insoluble residue is collected, ignited, weighed, and treated with hydrofluoric and sulphuric acids in the usual manner for silica.

The filtrate from the silica is precipitated cold with barium chloride, and the barium sulphate collected and weighed.

(*i*) *Phosphorus.*—One g. is dissolved as in (*h*), most of the hydrochloric acid being evaporated. The filtrate is rendered alkaline with ammonia, re-acidified with nitric acid, and treated with molybdate mixture. The phosphorus is determined as usual.

(*j*) *Manganese.*—One g. is dissolved in *aqua regia*, and the iron precipitated with sodium hydroxide. The precipitate is dissolved in hydrochloric acid, the iron precipitated with zinc oxide, and the filtrate tested for manganese as usual.

(*k*) *Carbon in Ferromolybdenum.*—By combustion in oxygen in an electric tube-furnace at 1200° C. and determination of the carbon dioxide by the usual method.

§ **X. Complete Analysis of Ores.**—(*a*) *Molybdenite Ores.*—The gangue usually consists of quartz, muscovite, and felspars. A small quantity of copper pyrites is often found; pyrites and mispickel may also be present. Native bismuth is an important constituent of certain ores, in which it is often accompanied by galena. It is necessary also to look for wolfram, scheelite, and cassiterite. Assuming an ore contained all the above minerals in addition to molybdenite and molybdite, the complete analysis will be carried out as follows:

(1) *First portion: insoluble and common metals.* One g. of the finely crushed ore is heated with 15 ml. of nitric acid until the molybdenite is oxidized, 15 ml. of 1 : 1 sulphuric acid is added, and the liquid evaporated to sulphuric fumes. The covered beaker is heated strongly for a quarter of an hour to decompose any wolfram present, and allowed to cool. When cold, 50 ml. of water is added, and the mixture heated to dissolve molybdic acid and allowed to stand overnight for the deposition of lead sulphate. The residue, $R^1$, is collected and washed with 5 per cent. by volume sulphuric acid and reserved. The filtrate is heated to 80° C., a rapid current of hydrogen sulphide passed through, the precipitate filtered off, and the remainder of the molybdenum removed from the filtrate by treatment with persulphate and hydrogen sulphide as in § IV, *c*. Iron, aluminium, titanium, manganese, calcium, and magnesium are determined in the filtrate in the usual manner. The sulphide precipitate is dissolved in nitric acid, and the

copper determined according to § IX, *b*, 1. The residue $R^1$ is extracted with hot ammonium acetate, and the lead determined in the filtrate. The insoluble fraction is heated with 100 ml. of 1 per cent. sodium hydroxide, 3 g. of ammonium nitrate added, and the solution boiled until feebly ammoniacal. The final residue (silica and gangue) is collected with the aid of filter-pulp, washed with ammonium nitrate, and ignited. It is resolved into its constituents by the usual methods of silicate analysis.

(2) *Second portion: molybdenum* is determined as under § VIII, *b*.

(3) *Third portion: sulphur.*[1] One g. of the powdered ore is fused with a mixture of 8 g. of anhydrous sodium carbonate and 4 g. of sodium peroxide in a covered nickel crucible. The fluid melt is poured out, disintegrated with water, the resulting solution boiled, cooled, and transferred to a 200-ml. graduated flask. After filtration through a dry pleated filter, 100 ml. of the clear filtrate is feebly acidified with hydrochloric acid, and the carbon dioxide boiled off. The neutralized solution is treated with 5 ml. of glacial acetic acid and 12·5 g. of ammonium acetate. After being diluted to about 350 ml., the solution is boiled and titrated dropwise with 4 per cent. lead acetate solution until it fails to give a colour with tannin solution on a spot plate (*cf.* § V, *b* and § IV, *a*, 2); ammonium molybdate solution (1·86 g. per 100 ml.) is then added until tannin once more gives a faint molybdate reaction. The solution is boiled for ten to fifteen minutes, the precipitate allowed to settle, collected and washed with 2 per cent. ammonium acetate, dissolved and reprecipitated as under § IV, *a*, 2, filtered off and washed as before.

The combined filtrates are evaporated in a litre beaker with hydrochloric acid for the expulsion of the acetic acid, 20 ml. of strong nitric acid is added, and the covered beaker heated until effervescence ceases. The cover is removed and the liquid evaporated to dryness on the water-bath. After two evaporations with hydrochloric acid, the residue is taken up with hydrochloric acid and the sulphuric acid precipitated with barium chloride as usual.[2]

(4) *Fourth portion: tungstic oxide.* As in § IX, *f*.

(5) *Fifth portion: bismuth, arsenic, antimony, and tin.* One to two g. of the ore is decomposed with nitric and sulphuric acids; excess of iron alum is added, and the solution precipitated with ammonia (§ III, *a*, 2 and *g*). The ferric hydroxide is dissolved in hydrochloric acid, and the usual methods of separation and determination of the above metals are applied. The tin may be present as cassiterite, in which case it will remain in the insoluble residue.

(6) *Sixth portion: molybdenum present as molybdite.* One to two g. of the ore is digested with warm 2 per cent. caustic soda, and the molybdenum in the filtrate determined after precipitation as sulphide from tartrate solution (§ VIII, *a*).

(7) *Seventh portion: alkalis.* One g. is roasted in a silica crucible, transferred to a platinum dish, and treated by Berzelius's hydrofluoric acid method.

(*b*) *Wulfenite Ores.*—In addition to wulfenite, these may contain vanadinite (*q.v.*, **XVII**, § I, *c*, 2); mimetite, $3Pb_3(AsO_4)_2.PbCl_2$; pyromorphite,

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[1] D. A. Lambie and W. R. Schoeller, *Analyst*, 1940, **65**, 284.

[2] A blank test should be carried out on the reagents.

$3Pb_3(PO_4)_2.PbCl_2$; and crocoisite, $PbCrO_4$. The summarized procedure is as follows:

(1) *First portion: insoluble and common metals.* One g. is attacked with nitric and sulphuric acids, and the insoluble residue, $R^1$, collected and reserved as under *a*, 1, *above*. Similarly, the metals of the hydrogen-sulphide group are precipitated, and the precipitate examined for copper. The filtrate is boiled for the removal of hydrogen sulphide, oxidized with nitric acid, and treated with a solution of 0·2 g. of ferric iron, which is precipitated as basic acetate, the filtrate being tested for calcium and magnesium. The precipitate, which contains aluminium, chromium, vanadium, and phosphorus, is dissolved in hydrochloric acid, tartaric acid added, and the iron precipitated as sulphide and discarded. The aluminium, vanadium, and chromium are recovered from the filtrate (after decomposition of ammonium sulphide by boiling) by precipitation with tannin and ammonium acetate. The tannin precipitate is treated as under **XVII,** § III, *h* and *j*.

The residue $R^1$ is boiled with ammonium carbonate, the solution filtered and discarded; the insoluble fraction is washed with dilute ammonium carbonate solution, extracted with nitric acid, and the filtered extract evaporated with sulphuric acid for the determination of the lead; the residue from the nitric-acid extraction is ignited and weighed as insoluble gangue, which may be analysed by the usual processes of silicate analysis if desired.

(2) *Second portion: molybdenum* is determined as under § VIII, *a*.

(3) *Third portion: tungstic oxide.* As in § IX, *f*.

(4) *Fourth portion: bismuth, arsenic, antimony, and tin.* As under *a*, 5, *above*, except that the lead sulphate is filtered off before the precipitation with ammonia. If much bismuth is present, the lead sulphate should be tested for bismuth.

(5) *Fifth portion: iron.* One g. is treated with nitric and sulphuric acids, and the lead removed as in the first portion. The iron is then separated from the molybdenum by precipitation with caustic soda as in § III, *a*, 1, the ferric hydroxide being dissolved in acid and the precipitation repeated. The iron is determined colorimetrically or by titration with permanganate, according to the amount present.

(6) *Sixth portion: chlorine.* One g. of the finely powdered ore is digested with 1 : 1 nitric acid at a temperature not exceeding 50° C. to complete decomposition. The solution is diluted, filtered, precipitated with silver nitrate, and the precipitate collected and weighed.

(7) *Seventh portion: phosphorus.* One g. is decomposed by treatment with *aqua regia*, and the solution evaporated with hydrochloric acid for removal of the nitrates. The bulk of the lead is filtered off as chloride. The filtrate is treated with hydrogen sulphide, and the precipitate of molybdenum, lead, and arsenic sulphides filtered off and discarded. The filtrate is evaporated with nitric acid to yield a nitrate solution, from which the phosphorus is precipitated with ammonium molybdate. If vanadium is present, the solution should be reduced with sulphur dioxide prior to precipitation with molybdate.

# XXI.—TUNGSTEN.

§ I. **Minerals.**—(*a*) *Monoclinic Tungstates.*—These are chiefly represented by the wolframite series, which comprises: (1) *ferberite*, ferrous tungstate; (2) *hübnerite*, manganous tungstate; (3) *wolframite*, an isomorphous mixture of the first two. In practice the distinction between the three is somewhat arbitrary, since ferberite usually contains some manganese tungstate and hübnerite some iron tungstate. According to Hess,[1] ferberite contains 80 to 100 per cent. $FeWO_4$ and 20 to 0 per cent. $MnWO_4$; hübnerite, 80 to 100 per cent. $MnWO_4$ and 20 to 0 per cent. $FeWO_4$; and wolframite, 20 to 80 per cent. $FeWO_4$ and 80 to 20 per cent. $MnWO_4$. All three are similar in appearance and lustre (distinctly sub-metallic on fresh cleavage planes); they are brittle and give an uneven fracture. Streak red to chocolate-brown (distinction from cassiterite, with which they are generally found); colour brown to black. H. 4·5 to 5·5; sp. gr. 6·8 to 7·5. Attracted by a strong electromagnet (*cf.* cassiterite). Finely powdered wolframite is soluble in hot strong hydrochloric acid, but is scarcely attacked by nitric acid.

(4) *Raspite*, lead tungstate, $PbWO_4$, occurs in small, brownish-yellow, tabular crystals.

(*b*) *Tetragonal Tungstates.*—(1) *Scheelite*, calcium tungstate, $CaWO_4$, is a white, more or less opaque, heavy mineral. H. 5; sp. gr. 6. An important ore of tungsten; it is often found with cassiterite. Hydrochloric acid dissolves powdered scheelite readily; nitric acid attacks it superficially, the particles becoming yellow through liberation of tungstic acid. It often contains a little molybdenum (*cf.* powellite, **XX,** § I, *d*).

(2) *Cuproscheelite*, $(Ca,Cu)WO_4$, is a variety of the preceding in which copper partly replaces calcium. Colour green, streak greenish-grey.

(3) *Stolzite*, lead tungstate, $PbWO_4$, is resinous and sub-translucent; colour grey, brown, or red. H. 3; sp. gr. 8. Isomorphous with wulfenite (*q.v.*, **XX,** § I, *b*).

(4) *Chillagite*, a variety of stolzite in which the tungsten is partly replaced by molybdenum.

(5) *Reinite* has the same composition as ferberite, and appears to be a pseudomorph of scheelite. Unimportant.

(*c*) (1) *Tungstic ochre* is an alteration product of wolframite, to which the formula $WO_3$ is usually assigned; but it generally contains a little ferric oxide and water. Colour usually bright yellow, but sometimes light brown or even white. Amorphous soft powder or incrustations.

(2) *Tungstenite*, tungsten sulphide, $WS_2$, closely resembles molybdenite (*q.v.*, **XX,** § I, *a*) in its physical properties; sp. gr. 7·4.

§ II. **Properties and Compounds.**—(*a*) The *element*, obtained by reduction of the trioxide with hydrogen at a bright red heat, is a very hard steel-grey metal of sp. gr. 19·3, melting above 3000° C. It is insoluble in all acids except a mixture of nitric and hydrofluoric, or perchloric and phosphoric acids. The powder dissolves in boiling caustic alkalis with formation of alkali tungstates and liberation of hydrogen.

(*b*) *Tungsten trioxide*, $WO_3$, is a canary-yellow heavy powder, soluble in caustic alkalis or hydrofluoric acid, but insoluble in hydrochloric, nitric, or sulphuric acid. It is obtained by ignition of tungstic acid or ammonium tungstate.[1]

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[1] F. L. Hess, *Bull. U.S. Geol. Surv.*, 1917, p. 652.

(*c*) *Tungstic Acids.*—Acids corresponding with three series of tungstates are known: *orthotungstates*, $M^I_2O.WO_3$; *metatungstates*, $M^I_2O.4WO_3$; and *paratungstates*, $5M^I_2O.12WO_3$ or $3M^I_2O.7WO_3$.

When a mineral acid is added to a cold solution of alkali tungstate, a white, amorphous precipitate of hydrated tungstic oxide, slightly soluble in water, is thrown down. Since its thermal decomposition curve gives no discontinuity, it is not considered to be a definite hydrate. If the hot normal-tungstate solution is treated with excess of mineral acid, a dense yellow precipitate of tungstic acid, $H_2WO_4$, is formed. This is insoluble in water but tends to form a hydrosol; it is soluble in ammonia.

*Metatungstic acid* may be extracted with ether from an aqueous solution of metatungstate acidified with hydrochloric acid. It forms colourless crystals, $H_2W_4O_{13}.9H_2O$, readily soluble in water and alcohol.

The *paratungstic acid* corresponding with salts of the formula $5M_2O.12WO_3$.aq. has been prepared in dilute aqueous solution by treatment of barium paratungstate with a slight deficiency of dilute sulphuric acid. The solution cannot be concentrated without decomposition, even *in vacuo*, and when boiled it deposits tungstic acid.

Tungstic acid combines with certain acidic oxides (*e.g.* silicic, boric, phosphoric, vanadic, arsenic, antimonic) to form heteropolytungstic acids, of which the following are typical examples: *borotungstic acid*, $B_2O_3.24WO_3.9H_2O$; *silicotungstic acid*, $SiO_2.12WO_3.4H_2O$; *phosphotungstic acid*, $P_2O_5.24WO_3.7H_2O$. The facility with which tungsten forms complex molecules is a source of possible error in analysis. For example, silicotungstates, most of which are soluble in water, are formed when solutions of metallic polytungstates are boiled with gelatinous silica; neither the silica nor the tungstic acid is precipitated from the complex by evaporation with hydrochloric acid.

(*d*) *Tungstates.*—In addition to the normal alkali tungstates, a large number of polytungstates have been prepared, in which the ratio $WO_3 : M^I_2O$ may be as high as 10.

The ordinary "*tungstate of soda*" of commerce is the paratungstate, $5Na_2O.12WO_3$.aq. It is prepared on the large scale from wolframite by fusion with soda-ash and lixiviation of the melt with water. The boiling solution is almost neutralized with hydrochloric acid and allowed to crystallize. If the partial neutralization with acid is omitted the orthotungstate, $Na_2WO_4.2H_2O$, crystallizes out.

*Ammonium tungstate*, $(NH_4)_2WO_4$, is obtained by solution of precipitated tungstic acid in ammonia, but it cannot be isolated in the solid state, the solution on evaporation depositing glittering plates of the paratungstate, $5(NH_4)_2O.12WO_3.11H_2O$ or $3(NH_4)_2O.7WO_3.6H_2O$.

(*e*) *Sulphides.*—When tungsten trioxide is dissolved in sodium sulphide a deep brown solution is obtained which contains the *thiotungstate*, $Na_2WS_4$, and which, on acidifying, yields a flocculent brown precipitate of *tungsten trisulphide*, $WS_3$. Tartaric or oxalic acid prevents the precipitation. The trisulphide is slightly soluble in water, giving a brown solution, and on ignition in an inert atmosphere yields the *disulphide*, $WS_2$. This bears a great resemblance to molybdenite (*q.v.*, **XX**, § I, *a*).

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[1] If a quantity of more than a few grams of this salt is ignited, the ammonia evolved partially reduces the tungstic oxide in the interior of the mass to a blue lower oxide.

§ **III. Quantitative Separation.**—The development of the analytical chemistry of tungsten in the last two decades is by no means commensurate with the increased use of the metal in the arts. Of the advances, the application of tannin to the determination of tungsten[1] is of major importance, since it provides for the rapid quantitative recovery of minute or large amounts of the element from solutions containing large quantities of alkali salts. Again, the magnesia method (**XVIII,** § III, *g*, 1), developed for the separation of tungsten from the earth acids, will no doubt find wider application. The detection of traces of tungsten, especially in the presence of a large excess of molybdenum, is still an unsolved problem.

Tungstic acid, being insoluble in mineral acids, is found in the ordinary course of analysis with the acid-insoluble residue (silica, gangue, etc.), but unless special precautions are taken the recovery is incomplete.

(*a*) *From Iron, Manganese, Calcium, and Heavy Metals.*—The tungstic acid is precipitated by means of *aqua regia*, cinchonine solution being added to recover any tungsten present as a soluble complex (§ IV, *b* and § VIII, *a*). According to Davis,[2] " the time of settling in the presence of considerable iron should not be less than twelve hours."

(*b*) *From Silica.*—(1) The weighed mixture of tungstic oxide and silica in a platinum crucible is moistened with 1 : 1 sulphuric acid, treated with a few ml. of hydrofluoric acid, and evaporated to dryness, care being taken to avoid loss of tungstic oxide by spattering. The crucible is ignited at 850° C., cooled, and again weighed. It is not possible by this means to determine both tungstic oxide and silica accurately in the same portion, since for complete dehydration of silica a temperature of 1000° C. must be exceeded, and sublimation of tungstic oxide begins at 800° C. (*cf.* footnote to § IV, *a*). If silica is to be determined, the oxides are ignited initially at 1000° to 1200° C., the silica volatilized as *above*, and the residue of tungstic acid ignited at 850° C. When the tungstic oxide greatly preponderates over the silica the latter should not be determined by difference as *above*, but by the following method:

(2) The tungstic oxide is fused with potassium bisulphate and the melt leached with a saturated solution of ammonium carbonate.[3] The residue is collected, washed with ammonium nitrate solution, ignited, weighed, and treated with sulphuric and hydrofluoric acids in the usual manner, the silica being taken by difference. The tungsten may be recovered from the filtrate if desired by means of tannin and cinchonine (§ IV, *c*).

(3) Tungstic acid precipitated by means of mineral acid is readily soluble in ammonia or ammonium carbonate solution. A small quantity (seldom exceeding 0·5 mg.) of silica is also dissolved. This may be recovered from the ignited tungstic acid as under (2), *above*. (For details see § VIII, *a*.)

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[1] W. R. Schoeller and C. Jahn, *Analyst*, 1927, **52**, 504.
[2] C. W. Davis, *Bull.* **212**, *U.S. Bur. Mines*, p. 161.
[3] H. Arnold, *Zeitsch. anorg. Chem.*, 1914, **88**, 333.

(*c*) *From Arsenic.*—(1) The arsenic is distilled off as trichloride after addition of a large excess of phosphoric acid to keep the tungstic acid in solution (§ IX, *b*, 2).[1]

(2) The arsenic is precipitated as sulphide from tartrate solution (§ IX, *b*, 1). It is essential for the formation of a stable tartarotungstic complex that the tartaric acid be added to the alkaline tungstate solution, not to an acid tartrate solution. Alternatively, after addition of the tartaric acid, the solution may be rendered alkaline and re-acidified.

(3) Arsenic may also be precipitated with magnesia mixture in ice-cold ammoniacal tartrate solution, the tartaric acid being kept to a minimum and a large excess (10- to 15-fold) of magnesia mixture used (*cf.* **XX,** § III, *c*, 2).

(*d*) *From Phosphorus.*—Phosphorus may be precipitated with magnesia mixture from ammoniacal tartrate solution (*cf. c*, 3, *above*, and **XX,** § III, *c*, 2). When only a trace of phosphorus is present the tartaric acid should be omitted, since it inhibits the precipitation (§ IX, *f*).

(*e*) *From Vanadium.*—See **XVII,** § III, *f*, 4 and *g*.

(*f*) *From Tin.*—(1) When the mixed oxides are fused with alkali carbonate and the solution of the melt boiled with excess of ammonium nitrate, stannic acid will be precipitated.[2] The tungsten may be recovered as in § IV, *c*.

(2) When present in the ore as cassiterite the tin will remain with the tungstic acid if the *aqua regia* method of attack is employed, and will remain undissolved when the residue is treated with ammonia.

(3) Tin may be precipitated with hydrogen sulphide from tartrate solution (§ IX, *a*, 2).

(*g*) *From Molybdenum.*—See § IX, *g*; also **XX,** § III, *j*.

(*h*) *From Silver.*—The ammoniacal tungstate solution is treated with ammonium sulphide, and the precipitated silver sulphide collected and determined as usual.

(*i*) *From Titania.*—See **XIII,** § III, *g*.

(*j*) *From the Earth Acids.*—See **XVIII,** § III, *g*.

(*k*) *From Aluminium.*—The mixed oxides are fused with potassium carbonate, and the solution of the melt treated by the magnesia method (see **XVIII,** § III, *g*, 1); the aluminium remains in the precipitate.

(*l*) *From Zirconia, Thoria, Rare Earths, Beryllia, and Ferric Oxide.*[3]—The mixed oxides are fused in a platinum crucible with sodium or potassium carbonate. If tungstic oxide predominates, 0·5 g. or more of the oxide is fused for fifteen minutes with 4 to 5 g. of alkali; whilst if zirconia (thoria) is in excess, a higher proportion of flux (3 to 6 g. for 0·1 to 0·3 g. of oxides) and a longer period of fusion (an hour), over a Méker or Teclu burner, should be employed. The cold melt is disintegrated with hot water, filter-pulp is stirred in, and the precipitate collected on a close-textured filter and washed with 2 per cent. alkali carbonate solution. The filter is returned to the beaker and pulped with hot water, the suspension acidified with hydrochloric acid, made slightly ammoniacal, and the precipitate again collected, washed with 2 per cent. ammonium nitrate solution, ignited, and weighed as zirconia, etc. The tungsten is determined in the filtrate (§ IV, *c*).

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[1] S. Hilpert and T. Dieckmann, *Ber.*, 1914, **47**, 2444.

[2] F. O. Bullnheimer, *J. Chem. Soc., Abs.*, 1901, **80**, 41.

[3] Schoeller, *op. cit.*, p. 92.

(*m*) *Testing Tungstic Oxide for Purity.*—Unless the ore is known to be free from molybdenum, arsenic, phosphorus, etc., it is advisable to test the weighed tungstic oxide (obtained as under § VIII, *a*) for impurities. The oxide is fused with about ten times its weight of potassium bisulphate, and the cold melt leached with a saturated solution of ammonium carbonate. The liquid is passed through a small filter, which is washed with 2 per cent. ammonium chloride solution, ignited, and weighed. This residue will probably be chiefly silica, which rarely amounts to 1 mg. The filtrate is treated with tartaric acid (twenty times the weight of tungstic oxide), acidified with 1 : 1 sulphuric acid, a few ml. of 10 per cent. potassium iodide solution added, and hydrogen sulphide passed in; any precipitate is collected and analysed. This may be either molybdenum sulphide or (rarely) silver sulphide; arsenic may also be present, although this is unusual with the small amounts of arsenic present in commercial concentrates. The filtrate is boiled for the removal of the hydrogen sulphide, made slightly alkaline with ammonia, cooled, and treated with a large excess of magnesia mixture (*d*, *above*). After being treated with 10 ml. of strong ammonia per 100 ml. of solution, it is cooled in ice, shaken well, and allowed to stand for twelve hours in ice. Any precipitate is collected and examined for phosphate. The sum of the impurities is subtracted from the weight of tungstic oxide.

§ **IV. Gravimetric Determination.**—Tungsten is weighed as trioxide, obtained as described *below*.

(*a*) *By Ignition of Ammonium Tungstate.*—A solution of ammonium tungstate free from other fixed constituents is evaporated to dryness in a tared porcelain or platinum dish, and the residue ignited, gently at first, then more strongly till pure yellow.[1]

(*b*) *By Precipitation with Mineral Acid.*—Tungstic acid is precipitated when tungstate solutions are boiled with excess of mineral acid, but precipitation is seldom, if ever, complete owing to the formation of small amounts of metatungstic acid or heteropolytungstic acids (§ II, *c*). Complete precipitation is, however, ensured by addition of cinchonine hydrochloride.

The alkali tungstate, or hydrochloric-acid solution obtained by acid attack of an ore (see § VIII, *a*), is evaporated to low bulk (10 ml.) and an equal volume of strong nitric acid added. The liquid is again evaporated to 5 ml., diluted to 50 ml. with hot water, and 5 ml. of 5 per cent. cinchonine solution [2] added. The liquid is set aside overnight before filtration. The precipitate is collected and washed with dilute cinchonine solution (60 ml. of cinchonine solution and 15 ml. of strong hydrochloric acid per litre), ignited, and weighed. In the presence of any considerable quantity of alkali salts, a protracted period of settling is required for complete deposition of the tungstic acid, but quantitative recovery is readily achieved in all cases by the use of method (*c*), *below*.

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[1] To ensure complete dehydration, the tungstic oxide should be heated above 750° C. Although the oxide begins to volatilize at 800° C., the loss does not become serious until 900° C. is exceeded, and in the final ignition of a precipitate a range of 750° to 850° C. is quite safe.

[2] Fifty g. of the alkaloid dissolved in 500 ml. of 1 : 1 hydrochloric acid, diluted to 1 litre with water, and filtered.

(*c*) *By Precipitation with Tannin and Cinchonine.*[1]—(1) *Not more than* 0·2 *g. of tungstic acid.* The alkaline tungstate solution is treated with 50 ml. of 20 per cent. ammonium chloride solution, diluted to 200 ml., heated to about 50° C., and treated with a freshly prepared solution of 0·5 to 2 g. of tannin in a little hot water (ten times as much tannin as the tungstic acid judged to be present, but not less than 0·5 g.). Hydrochloric acid (1 : 1) is added during agitation until the solution is acid to litmus-paper, then about 5 ml. in excess. The creamed pulp of half a 9-cm. Whatman No. 41 filter-paper is stirred in, followed by 5 ml. of 5 per cent. cinchonine solution[2] added dropwise with continuous stirring, which thoroughly blends the precipitated tungsten-tannin complex, filter-fibre, and cinchonine tannate. The beaker is set aside until cold, or cooled in running water. The precipitate is collected on a loose-textured filter (Whatman No. 41), washed 3 to 4 times with ammonium chloride-cinchonine solution,[3] returned to the beaker by a stream of wash-solution directed into the inverted funnel, stirred up with the same solution, again collected on the same filter, and the washing completed. Filter and precipitate are ignited wet in a tared porcelain crucible, finally over a Bunsen burner. The tungstic oxide should be of a pure yellow colour; a green oxide adhering to the crucible may be obtained if, owing to incomplete washing of the precipitate, alkali salts are still present.

(2) *More than* 0·2 *g. of tungstic acid.* Larger quantities of tungstic oxide than 0·2 g. give inconveniently bulky tannin precipitates, but by the following modification of the procedure this difficulty may be overcome. The feebly acid or alkaline solution is cautiously evaporated to 30 to 40 ml., treated with an equal volume of strong hydrochloric acid, and boiled until the precipitated tungstic acid turns yellow. After being diluted to 300 ml. with hot water, it is treated with a fresh solution of 0·5 g. of tannin, filter-pulp, and cinchonine as *above*. When cold, the liquid is filtered through a close-textured paper (Whatman No. 40) having a pad of filter-pulp in the apex. The washing is carried out with ammonium chloride-cinchonine solution as *above*. Any turbidity in the filtrate during washing may be ignored. Should a pellicle of tungstic acid adhere firmly to the beaker, it may be dissolved in a few ml. of ammonia and reprecipitated by addition of a little tannin, hydrochloric acid, filter-pulp, and cinchonine solution. It is convenient to do so before the bulk of the precipitate has been rinsed back into the beaker for washing. The precipitate is ignited wet in a tared porcelain crucible and weighed as $WO_3$.

§ V. **Volumetric Determination.**—No volumetric method for the determination of tungsten has yet found a place in analytical practice, the gravimetric processes being more reliable. Permanganate titration after reduction of the tungstate solution has been found to be unreliable.[4]

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[1] W. R. Schoeller and C. Jahn, *Analyst*, 1927, **52**, 504; D. A. Lambie, *ibid.*, 1939, **64**, 489.

[2] See footnote (2), p. 211.

[3] One hundred ml. of 20 per cent. ammonium chloride and 20 ml. of 5 per cent. cinchonine solution diluted to 1 litre with water.

[4] Hillebrand and Lundell, *op. cit.*, p. 551.

The acidimetric method based on solution of tungstic acid in a measured excess of standard alkali[1] or ethylamine[2] and back-titration with standard acid is less accurate than the gravimetric method, and involves the same operations for the separation of tungsten from its associates.

§ **VI. Colorimetric Determination.**—There is no method at present available for the colorimetric determination of tungsten in the presence of molybdenum. The following method[3] can be used in the absence of molybdenum and rhenium.

The material is fused with 1·3 g. of sodium carbonate, the melt dissolved in 15 ml. of water, the solution filtered if necessary, and made up to 50 ml. Twenty ml. is transferred to a 50-ml. graduated flask, treated with 2·5 ml. of 25 per cent. potassium thiocyanate solution, and made up to volume with a solution of 10 g. of stannous chloride in 90 ml. of strong hydrochloric acid. The yellow colour is matched after 45 to 60 minutes against those of a standard scale prepared at the same time from a sodium tungstate solution (0·0002 g. $WO_3$ per ml.) diluted to 20 ml. with 0·5N. sodium carbonate solution, and treated in the same manner as the unknown solution.

§ **VII. Detection in Ores.**—(*a*) All tungsten minerals on fusion with sodium carbonate, hydroxide, or peroxide, and extraction of the melt with water, yield a solution of sodium tungstate, which gives the following reactions:

(1) Hydrochloric acid in the cold produces a white flocculent precipitate of hydrated tungstic acid (*q.v.*, § II, *c*), which on boiling changes to the yellow anhydrous acid. Both precipitates are insoluble in acids but soluble in ammonia and alkalis. Phosphoric, arsenic, boric, tartaric, or oxalic acid prevents the precipitation.

(2) Addition of zinc and hydrochloric acid to a soluble tungstate produces a deep blue precipitate, or solution if phosphoric acid is present (*cf.* molybdenum, niobium, and vanadium).

(*b*) A particle of a tungstate mineral boiled with strong hydrochloric acid becomes coated with a bright yellow deposit of tungstic acid; the coating is soluble in ammonia or caustic soda.

(*c*) The finely ground ore (0·1 to 0·2 g.) is boiled with 1 to 2 ml. of strong hydrochloric acid and a small piece of lead foil for one or two minutes. In the presence of more than 0·5 per cent. of tungsten in the ore the solution becomes blue, and on being diluted gives a flocculent blue precipitate. The similar blue colour given by niobium disappears on dilution.[4]

§ **VIII. Determination in Ores and Alloys.**—*Methods of Attack.*—All tungsten minerals may be decomposed completely by treatment with hydrochloric and nitric acids as in (*a*), *below*, provided they are ground sufficiently fine (at least to pass a 200-mesh sieve). Ores, tungsten metal, and alloys may be obtained in solution by treatment with a mixture of hydrofluoric and nitric acids, silica being eliminated simultaneously (*c*, *below*). A mixture of perchloric and phosphoric acids is often of service in the analysis of alloys, giving as it does complete solution of tungsten metal, ferrotungsten, and tungsten steel (§ IX, *i*, 2).

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[1] F. Hundeshagen, *Chem. Zeit.*, 1894, **18**, 505.

[2] J. B. Ekeley and G. D. Kendall, *West. Chem. Met.*, 1908, **4**, 1.

[3] F. Feigl and P. Krumholz, *Angew. Chem.*, 1932, **45**, 674; J. A. Tschernichow and M. P. Karsajewskaja, *Zeitsch. anal. Chem.*, 1934, **98**, 97; Schoeller, *op. cit.*, p. 153.

[4] A. Petrovsky, *Zeitsch. anal. Chem.*, 1924, **77**, 268.

Fusion of the ore with alkali bisulphate and subsequent solution of the melt in tartaric acid gives a solution of tungstic acid and the metals. It is, however, troublesome to recover tungsten from tartrate solution; hence this procedure is not recommended for the actual tungsten determination. If the bisulphate melt is leached with water or dilute acid, the tungstic acid is divided between the solution and the precipitate, but with small quantities of tungsten or in the presence of certain other elements (*e.g.* titanium) the resultant solution may contain all the tungstic acid. Fusion with alkali carbonate, hydroxide, or peroxide and treatment of the melt with water results in a solution of the anions. This method is of use in the determination of impurities in the ore (arsenic, tin, phosphorus).

(*a*) *Aqua Regia-Ammonium Tungstate Method* (*suitable for high-grade ores and concentrates*).—One g. of ore ground to 200-mesh is weighed into a 250-ml. conical flask, 100 ml. of strong hydrochloric acid (sp. gr. 1·16) is added, and the flask agitated till the ore is thoroughly mixed with the acid, leaving no unwetted particles. The flask is heated on the boiling water-bath for an hour [1] with frequent agitation, which prevents the ore from adhering to the flask; should this occur, then the deposit should be dislodged with a glass rod, which is left in the flask. The tungsten mineral should now be in solution; a white or brownish-white residue may be quartz or cassiterite, whilst a black, somewhat flocculent residue will probably consist of sulphides (pyrites). The flask is transferred to a hot-plate and the acid solution evaporated to about 10 ml., 10 ml. of strong nitric acid is added, and the volume reduced to about 5 ml. The residue is taken up with 50 ml. of boiling water and 5 ml. of 5 per cent. cinchonine solution (p. 211, footnote 2). After standing overnight, the solution is decanted through a close-textured 9-cm. filter (Whatman No. 40) having a pulp pad in the apex, the precipitate being retained as far as possible in the flask, and being washed by decantation with dilute cinchonine solution.[2]

Filter and precipitate should be washed free from iron. The flask and filter are given one wash with 1 per cent. hydrochloric acid to displace the excess of cinchonine. The flask is then rinsed round with ammonia wash-solution,[3] 5 ml. of strong ammonia added, and the tungstic acid dissolved by warming. The solution is filtered through the same paper, the filtrate being received in a tared porcelain or platinum dish; filter and flask are washed with the ammonia wash-solution. The filtrate, which now contains the greater part of the tungstic acid as ammonium tungstate, is evaporated to dryness on the water-bath, the residue gently heated until the ammonium salts are driven off, finally ignited over a Bunsen burner, and weighed as $WO_3$ (§ IV, *a*).

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[1] It is important to avoid loss of hydrochloric acid at this stage, or incomplete solution of the tungsten mineral may result.

[2] Fifteen ml. of strong hydrochloric acid and 60 ml. of 5 per cent. cinchonine solution diluted to 1 litre with water.

[3] Fifty ml. of ammonium hydroxide (sp. gr. 0·88) and 25 ml. of 20 per cent. ammonium chloride diluted to 1 litre with water.

The residue from the ammonia extraction may contain appreciable amounts of tungstic acid, especially if titania and earth acids are present, and if owing to insufficiently fine grinding the ore has not been completely attacked by the acid treatment. The residue should be transferred completely to the filter (most readily by means of filter-pulp and a rubber-tipped glass rod) and ignited in a porcelain crucible, unless tin is known to be absent, when a platinum crucible may be employed. It is treated in a platinum crucible with two drops of 1 : 1 sulphuric acid and a few ml. of hydrofluoric acid, and evaporated to dryness. The residue is ignited and fused with 4 g. of potassium carbonate. The cold melt is leached with about 150 ml. of water, and the resulting liquid treated by the magnesia method (**XVIII,** § III, *g*, 1). After standing for half an hour on the water-bath, the solution is filtered and the precipitate washed with hot 2 per cent. ammonium chloride solution. The tungstic acid is recovered from the filtrate with tannin and cinchonine (§ IV, *c*). Unless the material is known to be very pure, the combined tungstic oxide residues should be tested for impurities as in § III, *m*.

(*b*) *Tannin-Cinchonine Method* (*suitable for low-grade ores*).—One to five g. of the finely ground ore, according to the anticipated tungsten content (less than 0·2 g. $WO_3$), is weighed into a 250-ml. conical flask. The attack and preliminary treatment (including the addition of 5 ml. of cinchonine solution) are the same in this method as in (*a*), *above*. After standing overnight, the precipitate is collected on a close-textured filter-paper (Whatman No. 40) having a pulp pad in the apex, and washed with the dilute cinchonine solution.[1] The filter containing the residue is transferred to the flask, pulped with about 40 ml. of hot water, and 4 g. of sodium hydroxide added. The mixture is digested for a quarter of an hour on a hot-plate, treated with a solution of 1 g. of magnesium sulphate in 50 ml. of 20 per cent. ammonium chloride solution, and the digestion continued for half an hour. The precipitate is filtered off, washed thoroughly with hot 2 per cent. ammonium chloride solution, and discarded. The filtrate is treated by the tannin-cinchonine process for tungsten (§ IV, *c*).

(*c*) *Hydrofluoric Acid Method* (*suitable for high-grade ores, concentrates, or ferrotungsten*).—One g. of the material is treated in a weighed platinum dish with hydrofluoric and nitric acids (since the reaction is very vigorous with ferrotungsten, the nitric acid should be added cautiously by means of a glass tube) followed by 10 ml. of 1 : 1 sulphuric acid. The mixture is heated cautiously until the acids have evaporated, and the residue taken up with 5 ml. of hydrochloric acid and 50 ml. of hot water, being heated until the sulphates are dissolved; at this stage 5 ml. of 5 per cent. cinchonine solution is added. The precipitate is allowed to settle overnight, collected, and washed with dilute cinchonine solution.[1] Filter and precipitate are ignited in the original platinum dish, and weighed. The tungstic oxide is fused with sodium carbonate, and leached with water; any precipitate is collected, washed with ammonium nitrate solution, ignited, and weighed in the platinum dish, tungstic oxide being taken by difference. The tungstate solution may be examined for impurities as in § III, *m*.

[1] See footnote (2), p. 214.

(*d*) *Caustic Soda Method* [1] (*for low-grade ores, but inapplicable to scheelite*).—Five to ten g. of the finely powdered ore is heated for 45 minutes with 20 ml. of 25 per cent. caustic soda solution in a porcelain dish. A little sodium peroxide is added to oxidize sulphides, the solution diluted to 200 ml., and boiled with excess of ammonium nitrate. It is cooled and rinsed into a 250-ml. graduated flask, made up to volume, mixed, and poured through a dry filter. The tungsten is determined in 200 ml. of filtrate by the tannin-cinchonine method (§ IV, *c*).

**§ IX. Determination of Impurities in Ores and Ferrotungsten.**—The most objectionable impurities commonly met with in tungsten ores are tin, arsenic, bismuth, copper, sulphur, and phosphorus.

(*a*) *Tin*, the most important impurity, is almost invariably present. While it is not so objectionable in wolfram ores, from which it can be eliminated by electromagnetic separation, it is a more harmful constituent of scheelite ores. The tin may occur as cassiterite or stannine, or both; the methods given *below* are applicable in every case.

(1) *Bisulphate-tartaric method.*[2] One g. of finely crushed ore is fused in a silica crucible with 5 g. of dehydrated potassium bisulphate. The melt is leached with a solution of 10 g. of tartaric acid, rendered alkaline with caustic soda solution, and re-acidified with 1 : 1 sulphuric acid. The solution (about 200 ml.), warmed to 50° to 60° C., is treated with 5 ml. of 10 per cent. potassium iodide solution and a current of hydrogen sulphide. Residue and precipitate are collected on a filter with the aid of filter-pulp, washed with 5 per cent. sulphuric acid containing hydrogen sulphide, ignited gently in an iron crucible, fused with sodium peroxide, and the determination finished as usual.

(2) *Sodium peroxide method.* 2·5 g. of the ore or alloy is fused in an iron crucible with 10 g. of sodium peroxide, the fluid melt poured out, left to cool, and disintegrated with water; the liquid is boiled for a few minutes, cooled, and transferred to a 250-ml. graduated flask. The solution is made up to volume, mixed thoroughly, and filtered through a dry pleated filter (Whatman No. 50); 100 ml. of filtrate is treated with 15 g. of tartaric acid, 5 ml. of 10 per cent. potassium iodide solution, and 5 ml. of 1 : 1 sulphuric acid, diluted to 200 ml., and saturated at 60° C. with hydrogen sulphide. After the solution has been heated for the coagulation of the precipitate, the gas is passed for a few minutes longer, the precipitate collected, and washed with 5 per cent. sulphuric acid containing hydrogen sulphide. The sulphide precipitate is returned to the original beaker, being rinsed off the filter-paper with water and a little dilute sodium polysulphide solution. The liquid is treated with 20 ml. of 1 : 1 sulphuric acid and evaporated till it fumes and turns colourless. When cold it is diluted with 15 ml. of cold water, cooled, 40 ml. of strong hydrochloric acid added, and the arsenic precipitated with hydrogen sulphide. Ten ml. of cold water is added slowly with stirring, the precipitate collected (a Whatman No. 1 filter may be used), and washed with 1 : 1 hydrochloric acid. The tin is recovered from the filtrate, after partial neutralization, with hydrogen sulphide, and estimated in the usual manner.

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[1] H. W. Hutchin and F. J. Tonks, *Analyst*, 1909, **34**, 457; *Trans. Inst. Min. Met.*, 1909, **18**, 425.

[2] A. R. Powell, *J. Soc. Chem. Ind.*, 1918, **37**, 285.

(*b*) *Arsenic* is, next to tin, the most frequent impurity. It occurs either as mispickel or as a ferric arsenate, or as both. The arsenate is very often insoluble in nitric acid, but soluble in hydrochloric acid, and hence cannot be readily separated from wolfram by a selective attack. The last method here described, (3), *below*, is not applicable to ores containing arsenate.

(1) The method *a*, 2 for tin may also be used for the determination of arsenic,[1] the arsenic sulphide precipitate, after having been washed with 1 : 1 hydrochloric acid, being washed with 5 per cent. sulphuric acid until free from chlorides; the precipitate is dissolved and titrated with iodine as usual.

(2) *Distillation method.* The ore is fused with sodium peroxide, the melt taken up with water, and an aliquot portion (100 ml.) of the filtrate taken as under *a*, 2. It is transferred to a 500-ml. distillation flask fitted with a suitable condenser and receiver, and 20 ml. of syrupy phosphoric acid added (a few small pieces of pumice also should be added, to promote smooth ebullition). The water is distilled off until about 40 ml. of liquid remains in the flask. A concentrated solution of 5 g. of potassium iodide or cuprous chloride and 50 ml. of strong hydrochloric acid are added, and the distillation is continued until the volume is again reduced to 40 ml. The distillation is repeated with a further 50 ml. of strong hydrochloric acid. The arsenic is recovered from the distillate with hydrogen sulphide and determined as usual.

(3) *Acid attack.* From 1 to 20 g. of ore, according to the arsenic content, is treated with 20 ml. of strong nitric acid and 1 ml. of bromine at 50° to 60° C. for about an hour. The acid is then boiled down to about 10 ml., diluted with 50 ml. of hot water, filtered, and the filtrate precipitated with an excess of ammonia. (If this does not produce a reasonably large precipitate of ferric hydroxide a little ferric chloride should be added to the acid solution, followed by an excess of ammonia.) The precipitate, containing all the arsenic, is filtered off, washed free from nitrates with 2 per cent. ammonium chloride, dissolved in hydrochloric acid, and the assay reduced with an excess of stannous chloride. Twice the volume of strong hydrochloric acid is added, the arsenic precipitated with hydrogen sulphide, the precipitate filtered and washed, first with 1 : 1 hydrochloric acid until free from tin, then with 5 per cent. sulphuric acid till free from chlorides. It is then dissolved and titrated with iodine. Alternatively, the ferric hydroxide precipitate may be distilled with concentrated hydrochloric acid and ferrous chloride, and the distillate titrated with iodine as usual.

(*c*) *Bismuth* is usually present in very small quantities, in which case it is best determined colorimetrically.

(1) One g. of ore is digested for ten to fifteen minutes with 10 ml. of 1 : 1 nitric acid, the acid boiled nearly to dryness, and the residue taken up with 50 ml. of 1 : 4 sulphuric acid. The solution is transferred by decantation to a 250-ml. flask and diluted to the mark. Twenty-five ml. is filtered off into a Nessler tube, 3 ml. of 50 per cent. potassium iodide added, and then a 0·5 per cent. solution of sodium sulphite drop by drop until the colour ceases to fade. The solution in the tube is then made up to the mark (50 ml.) and

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[1] If molybdenum is present, method (2) should be used.

compared with a standard tube containing 5 ml. of 1 : 4 sulphuric acid, 3 ml. of potassium iodide solution, and a few drops of the sodium sulphite in 50 ml. of solution. A bismuth solution containing 0·1 g. of bismuth per litre is now added drop by drop to the standard tube till the tints match. One ml. of the standard bismuth solution is equivalent to 0·1 per cent. of bismuth in 0·1 g. of the ore taken.

(2) If much bismuth is present, it is extracted from the ore by digestion with nitric acid, the insoluble residue filtered off, the filtrate diluted considerably, and the bismuth precipitated in the cold by hydrogen sulphide; the precipitate is digested with sodium sulphide, then with potassium cyanide, dissolved in nitric acid, and the bismuth precipitated as oxychloride or phosphate.[1]

(*d*) *Copper.*—(1) *In ores.* The ore is digested with nitric acid, the wolfram filtered off, and the copper in the filtrate precipitated in the cold by hydrogen sulphide. The precipitate is ignited, dissolved in nitric acid, and the assay finished by any of the usual methods. If only small quantities are present, ammonia is added without filtering off the wolfram, and the copper determined colorimetrically in an aliquot portion of the filtrate.

(2) *In ferrotungsten.* One g. is treated as in § VIII, *c* for the removal of the tungsten. The copper is precipitated with hydrogen sulphide from the filtrate and determined by the usual methods.

(*e*) *Sulphur.*—(1) *In ores.* The ore is digested with nitric acid and potassium chlorate until all the sulphur has dissolved. The unattacked wolfram is filtered off, the filtrate evaporated to dryness, the nitric acid destroyed by two evaporations with hydrochloric acid, the iron removed with ammonia, and the sulphur precipitated in the acidified filtrate with barium chloride in the usual manner.

(2) *In ferrotungsten.* One g. is fused with sodium peroxide, the melt dissolved in hydrochloric acid, and the solution evaporated to dryness in a porcelain dish. The residue is taken up with dilute hydrochloric acid and treated with a few ml. of cinchonine solution. It is filtered with the aid of pulp, and the filtrate precipitated in the cold with barium chloride. A blank test should be carried out on the reagents.

(*f*) *Phosphorus.*[2]—2·5 to 5 g. of the finely powdered material is fused with sodium peroxide in a nickel crucible. The melt is taken up with water and the liquid transferred to a graduated flask. A suitable aliquot portion of the filtered solution is acidified with hydrochloric acid, and boiled until the carbon dioxide is removed. Any precipitated tungstic acid is dissolved by the addition of ammonia. The cold solution is treated with magnesia mixture, and left for at least six hours. The precipitate is collected, washed with 5 per cent. ammonia, dissolved in hydrochloric acid, and treated with hydrogen sulphide for the removal of arsenic and tin. The filtrate is evaporated to dryness, the residue taken up with nitric acid, and the phosphorus precipitated with molybdate mixture and determined as usual.

(*g*) *Molybdenum.*—2·5 g. of the material is fused with sodium peroxide and treated as under *a*, 2, *above*, for the recovery of the sulphides of tin, arsenic, and molybdenum. Unless an abnormally large amount of molybdenum is present, a rapid stream of hydrogen sulphide should precipitate it completely from hot solution. The precipitate is dissolved in *aqua regia*, and the solution precipitated with ferric salt and ammonia as under **XX,** § III, *g*. The molybdenum is determined in the filtrate as lead molybdate (see **XX,** § IV, *a*), or colorimetrically after precipitation as sulphide.

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[1] W. R. Schoeller and D. A. Lambie, *Analyst*, 1937, **62**, 534.

[2] After *Ausgew. Methoden*, p. 422.

(*h*) *Chromium, Aluminium, and Vanadium in Ferrotungsten.*—One g. is treated as in *d*, 2, *above*, and after removal of the tungsten and hydrogen-sulphide metals, tartaric acid and ammonium sulphide are added. After filtering off the ferrous sulphide, chromium, aluminium, and vanadium are recovered from the solution with tannin (see **XX,** § IX, *g*).

(*i*) *Manganese in Ferrotungsten.*—(1) One g. is treated as in § VIII, *c*; the filtrate from the tungstic oxide is almost neutralized with sodium hydroxide, treated with an excess of an aqueous suspension of zinc oxide, transferred to a graduated flask, made up to volume, mixed, and passed through a dry filter. A suitable aliquot portion is evaporated with sulphuric acid until white fumes are evolved, for the removal of chlorides. The manganese is estimated colorimetrically with persulphate or periodate.

(2)[1] One g. of finely divided material is weighed into a 500-ml. conical flask fitted with a refluxing head,[2] and treated with 30 ml. of a mixture of 1 part of 72 per cent. perchloric acid and 2 parts of 85 per cent. phosphoric acid. The mixture is heated gradually to 200° to 215° C., and maintained at that temperature until the material has dissolved (45 to 60 minutes). The resulting solution is cooled, diluted to 200 ml. with water, and boiled gently for a quarter of an hour after addition of 0·3 g. of potassium periodate (this is sufficient to oxidize 15 mg. of manganese to permanganic acid). It is then cooled and treated with a solution of 4 to 5 g. of mercuric nitrate in water to precipitate the excess periodate and iodate:

$$2KIO_4 + 5Hg(NO_3)_2 + 4H_2O = Hg_5(IO_6)_2 + 2KNO_3 + 8HNO_3.$$

The precipitate is collected on asbestos by suction and washed four times with water; the filtrate is received in a measured excess of standard ferrous sulphate solution, the excess being determined by titration with standard potassium permanganate solution.

(*j*) *Silicon in Ferrotungsten.*—0·5 g. is fused for one hour with 4 g. of potassium bisulphate at a low temperature. The melt is cooled, and re-fused after addition of a few ml. of strong sulphuric acid. The cold melt is dissolved in a solution of 6 g. of tartaric acid, the solution boiled and filtered with the aid of filter-pulp, and the filter washed with 1 per cent. sulphuric acid. The residue is ignited, fused with bisulphate, and the treatment repeated, the second residue being ignited, weighed, and treated with hydrofluoric acid in the usual manner for silica.

§ **X. Complete Analysis of Ores.**—The complete analysis of high-grade wolfram and scheelite concentrates is often required in connection with the manufacture of tungsten. A scheme for such an analysis is given *below*.

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[1] G. F. Smith, J. A. McHard, and K. L. Olsen, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8,** 350.

[2] See *Mixed Perchloric, Sulphuric, and Phosphoric Acids and their Application in Analysis*, G. F. Smith Chemical Co., Columbus, Ohio, 1935.

(*a*) *First Portion: Tungstic Oxide, Silica, and Base Metals.*—One g. is treated according to § VIII, *a*, the treatment resulting in three fractions:

(1) The ammoniacal filtrate containing the major tungsten fraction is evaporated and the residue ignited to $WO_3$, which is weighed.

(2) The insoluble residue from the ammonia extraction is ignited in a porcelain crucible, weighed, and treated with sulphuric and hydrofluoric acids in a tared platinum crucible, silica being determined by difference. The fixed residue is fused with potassium carbonate, and the solution of the melt treated by the magnesia method (**XVIII,** § III, *g*, 1) for the minor tungsten fraction.

The magnesia precipitate is ignited, fused with bisulphate, the melt dissolved in tartaric acid solution, the hot liquid saturated with hydrogen sulphide (**XVIII,** § III, *a*, 2), and set aside overnight. The filtered solution is precipitated with tannin as under **XVIII,** § IV, *b*, 2), and the coloured precipitate (if any) ignited and weighed as $(Nb,Ta)_2O_5 + TiO_2$. In commercial work it is as a rule unnecessary to determine these separately.[1]

(3) The cold acid filtrate containing the base metals is saturated with hydrogen sulphide, and the precipitate collected and analysed for lead, bismuth, and copper.

The filtrate from the sulphides is freed from hydrogen sulphide by boiling (the nitric acid present oxidizing the iron), treated with ammonium chloride and ammonia, boiled, and filtered. The precipitate, which contains cinchonine, is ignited, dissolved in hydrochloric acid, and the solution treated by Brunck's basic acetate method [2]; the precipitate is analysed for iron and aluminium (traces of titanium), while the filtrate is added to the filtrate from the ammonia precipitate. The combined solutions contain manganese, lime, and possibly magnesia.

(*b*) *Second Portion: Arsenic and Tin.*—See § IX, *a*, 2.

(*c*) *Third Portion: Sulphur.*—See § IX, *e*, 1.

(*d*) *Fourth Portion: Molybdenum.*—See § IX, *g*.

(*e*) *Fifth Portion: Phosphorus.*—See § IX, *f*.

## XXII.—URANIUM.

§ **I. Minerals.**—All uranium minerals are radioactive.

(*a*) *Oxides and Carbonates.*—(1) *Uraninite*, a complex mixture of oxides, described by Dana[3] as "a uranate of uranyl, lead, usually thorium (or zirconium), often the metals of the lanthanum and yttrium groups; also contains nitrogen in varying amounts up to 2·6 per cent." A black, pitch-like, heavy mineral; sp. gr. 9·5; H. 5·5. Non-magnetic; brittle; conchoidal fracture. Cubic, sometimes found as octahedra. Streak brown-black to olive-green and shining. There are several varieties of this mineral: *cleveite* contains about 10 per cent. of yttria earths; *bröggerite* shows a ratio of $UO_3$ to other bases of about 1 : 1; *uranoniobite* contains much thoria and the maximum observed amount of nitrogen.

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[1] For the determination of niobium and tantalum in wolframite, see J. A. Tschernichow and M. P. Karsajewskaja, *Zeitsch. anal. Chem.*, 1934, **98**, 97; Schoeller, *op. cit.*, p. 152.

[2] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 8th edition, 1935, **2**, 159.

[3] E. S. Dana, *Descriptive Mineralogy*, 6th edition, p. 890.

(2) *Pitchblende* is a black, amorphous, hydrated oxide containing only traces of thoria and rare earths; sp. gr. 6·5. It is found in veins with sulphide minerals, while uraninite occurs in pegmatitès.

(3) *Rutherfordine*, uranyl carbonate, $UO_2CO_3$, is a yellow, strongly radioactive alteration product of uraninite.

(4) *Uranothallite*, $U(CO_3)_2.2CaCO_3.10H_2O$, and *liebigite*, $UO_2CO_3.CaCO_3.20H_2O$, are varieties of uranium calcium carbonate. They are both soft (H. 2), green, translucent minerals having a vitreous to pearly fracture.

(*b*) *Silicates.*—(1) *Uranophane*, hydrous uranyl calcium silicate, $UO_3.CaO.2SiO_2.6H_2O$, occurs as minute acicular prisms in stellate or radiated aggregates, or massive with a fibrous structure. It is a honey-coloured, soft (H. 2·5) mineral with a vitreous to pearly lustre. Sp. gr. 3·8.

(2) *Thorogummite*, $UO_3.3ThO_2.3SiO_2.6H_2O$, is a dull yellow-brown, hydrous silicate of uranyl and thoria crystallizing in the tetragonal system; the crystals resemble those of zircon (*q.v.*, **XIV,** § I, *b*, 1). H. 4·5; sp. gr. 4·5.

(3) *Yttrogummite* is a translucent black mineral with a brilliant lustre and conchoidal fracture; it consists of a silicate of uranyl, thoria, and yttria.

(*c*) *Phosphates and Arsenates of Uranyl and Copper, Lime, or Baryta: General Formula* $M^{II}O.2UO_3.P_2O_5.8H_2O$.—(1) *Torbernite* (*copper uranite*), copper uranyl phosphate (H. 2·5; sp. gr. 3·5), is a brittle emerald-green mineral with a pearly to adamantine lustre and micaceous cleavage. Tetragonal, occurring in thin, transparent tables or in micaceous aggregates.

(2) *Zeunerite* is the arsenic analogue of torbernite, which it closely resembles; though the cleavage is perfect it is not micaceous.

(3) *Autunite* (*lime uranite*), calcium uranyl phosphate, occurs as thin tables or micaceous aggregates of a lemon-yellow colour giving a pale yellow streak. Perfect basal cleavage, and pearly lustre on cleavage faces. It is easily split up into brittle laminæ; orthorhombic; usually transparent to translucent. H. 2·5; sp. gr. 3·1.

(4) *Uranospinite*, the arsenic analogue of autunite, crystallizes in green rectangular tables belonging to the orthorhombic system. H. 2·5; sp. gr. 3·4. In other respects it resembles autunite.

(5) *Uranocircite* is autunite in which calcium is replaced by barium. Yellow-green mineral; sp. gr. 3·5; resembles autunite.

(*d*) *Other Phosphates and Arsenates.*—(1) *Phosphuranylite*, $(UO_2)_3(PO_4)_2.6H_2O$, forms deep lemon-yellow incrustations consisting of minute rectangular crystals with a pearly lustre.

(2) *Trögerite*, $(UO_2)_3(AsO_4)_2.12H_2O$, occurs as thin, yellow, monoclinic tables with a pearly lustre and perfect cleavage. Sp. gr. 3·3.

(3) *Walpurgite* is a yellow basic bismuth uranyl arsenate occurring in thin triclinic cleavable scales with a greasy lustre; often twinned.

(*e*) *Other Minerals.*—(1) *Uranosphaerite* is a hydrous bismuth uranate found in greasy, orange, globular aggregates of radiated concentric crystals. Streak yellow. H. 2; sp. gr. 6·4.

(2) Uranium is also found in minerals (*e.g. uranic ochre* and *zippeite*)

consisting of basic uranyl sulphates with copper or lime or both, resulting from the decomposition of other uranium minerals, especially uraninite and its varieties.

(3) *Carnotite* and other vanadates. See **XVII,** § I, *d.*

(4) Many titanoniobates, and minerals containing thoria and rare earths (*q.v.*), contain uranium.

§ **II. Properties and Compounds.**—(*a*) The *metal* is obtained by reducing the oxide $U_3O_8$ with carbon in the electric furnace. It is white, and readily combines with oxygen, the halogens, sulphur, and nitrogen. As a fine powder it decomposes cold water. The element and all its compounds are radioactive. Sp. gr. 18·7; m.p. 1500° C.

(*b*) *Uranium dioxide*, $UO_2$, is a brown powder formed by heating the oxide $U_3O_8$ in hydrogen. It has a sp. gr. of 10·15 and is soluble in strong sulphuric acid, giving uranous sulphate, $U(SO_4)_2.9H_2O$; strong nitric acid dissolves it to uranyl nitrate, $UO_2(NO_3)_2.6H_2O$; *aqua regia* converts it into uranyl chloride, $UO_2Cl_2.H_2O$. From fused borax it crystallizes in black octahedra isomorphous with thoria (*q.v.*, **XV,** § II, *b*).

(*c*) *Uranoso-uranic oxide*, $U_3O_8$, is a satiny, dark green powder formed by ignition of ammonium uranate, uranyl nitrate or carbonate, or any of the other oxides of uranium in air. Sp. gr. 7·2. Soluble in strong nitric or sulphuric, more difficultly so in hydrochloric, acid.

(*d*) *Ammonium diuranate*, $(NH_4)_2U_2O_7$, is an amorphous, deep yellow precipitate formed by adding ammonia to a uranyl salt. Soluble in acids. On ignition in air it leaves $U_3O_8$.

(*e*) *Sodium diuranate*, $Na_2U_2O_7$, is a yellow to orange precipitate produced by caustic soda in solutions of uranyl salts.

(*f*) *Uranyl nitrate*, $UO_2(NO_3)_2.6H_2O$, is formed by dissolving any oxide of uranium in nitric acid. It crystallizes as lemon-yellow, fluorescent, rhombic prisms, readily soluble in water, alcohol, or ether.

(*g*) *Uranyl ammonium phosphate*, $UO_2NH_4PO_4$, is a greenish-yellow amorphous precipitate insoluble in acetic acid, obtained by mixing uranyl acetate with ammonium chloride and sodium phosphate solutions. On ignition it gives uranyl pyrophosphate, $(UO_2)_2P_2O_7$.

(*h*) *Uranyl ammonium carbonate*, $UO_2CO_3.2(NH_4)_2CO_3$, is very soluble in water, and is formed by adding excess of ammonium carbonate to solutions of uranyl salts. The corresponding sodium and potassium compounds are obtained in the same manner, and are also soluble in water.

(*i*) *Uranyl ferrocyanide* is a red-brown amorphous precipitate closely resembling copper ferrocyanide.

(*j*) *Uranyl sulphide*, $UO_2S$, is precipitated from neutral uranyl salt solutions by ammonium sulphide. It is a brown precipitate insoluble in ammonia (distinction from vanadium), but soluble in ammonium carbonate and in acids.

(*k*) The *tannin complex* is obtained as a dark brown flocculent precipitate by addition of tannin to neutral tartrate or ammoniacal oxalate solutions of uranyl salts.

§ **III. Quantitative Separation.**—Whilst no recent radical changes have been introduced into the analytical chemistry of an element of such well-defined individuality as uranium, interest in the question of its accurate determination in minerals received a fresh stimulus through the increased demand for radium. Uranium is the parent substance of radium, and since the rate of disintegration of uranium has been accurately determined, it is possible to compute the radium content of unaltered uranium minerals by calculation based upon the uranium content, the following formula being used:

$$\text{Per cent. U} \times 3{\cdot}4 = \text{mg. Ra per ton.}$$ [1]

In the general analytical procedure, uranium is quantitatively precipitated by ammonia as yellow ammonium uranate, along with iron, aluminium, and other members of the third qualitative group; but it readily forms soluble complex alkali carbonates, hence its precipitation by ammonia and other reagents is prevented by the presence of alkali carbonates in the solution. The precipitation of brown uranyl sulphide by ammonium sulphide does not take place in the presence of alkali carbonate; tartrates prevent the precipitation both of uranyl sulphide and of ammonium uranate. The precipitation of uranium as phosphate is inhibited by ammonium carbonate, and that of ammonium uranate by ammonium oxalate.

The following reactions of uranium have been placed at the analyst's disposal as the result of more recent work, in which American investigators have taken a prominent part: Cupferron is a valuable reagent available for important separations: it precipitates iron, vanadium, titanium, and zirconium, but not sexivalent uranium, from mineral acid solution; and while it quantitatively precipitates quadrivalent uranium, it does not precipitate aluminium, manganese, beryllium, and other bivalent metals. Glacial acetic acid containing one-twentieth of its volume of nitric acid is a selective solvent for uranyl oxide of great utility in the assay of vanadiferous ores. Tannin has proved a convenient precipitant, especially for subordinate quantities of uranium: quantitative recovery is achieved from feebly ammoniacal acetate, tartrate, or oxalate solution, uranium taking its place amongst the members of Tannin Group B (*cf.* **XIII,** § III). Tannin precipitates uranium also from complex carbonate solution.

(*a*) *From Metals of the Hydrogen-sulphide Group.*—The solution, containing 5 per cent. by volume of strong hydrochloric acid, is treated with hydrogen sulphide. Uranium by itself is not precipitated, but shows a tendency to be occluded in the sulphide precipitate; hence for substantial quantities of the reacting metals it is advisable to dissolve the washed sulphide precipitate in acid and repeat the precipitation. The addition of tartaric acid prevents the coprecipitation of uranium,[2] which can be recovered from the filtrate by tannin precipitation (§ IV, *b*, 2). Lead is best separated from uranium as sulphate, the nitrate solution being evaporated with sulphuric acid in the usual manner; the last traces of lead must be precipitated by ammonium sulphide in presence of excess of ammonium carbonate (***b*, below**).

(***b***) ***From Iron, Titanium, Cobalt, Zinc, and Manganese: Ammonium Sulphide-***

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[1] L. D. Roberts, in W. W. Scott's *Standard Methods of Chemical Analysis*, 5th edition, New York, 1939, **1**, 767.

[2] Hillebrand and Lundell, *op. cit.*, p. 366.

*Ammonium Carbonate Method.*—The solution (100 ml.) contained in a conical flask is treated with excess of ammonia, 5 g. of ammonium carbonate, and a sufficiency of ammonium sulphide; the flask is corked and set aside overnight. The precipitate is collected and washed with water containing ammonium carbonate and sulphide; if bulky it should be dissolved and the precipitation repeated. The combined filtrate is boiled until the ammonium carbonate is decomposed, acidified with hydrochloric acid, again boiled till free from hydrogen sulphide, and the uranium precipitated with ammonia. The precipitate may contain beryllium, phosphorus, and small quantities of aluminium and zirconium. If nickel is present, the method given under (*c*) is preferable.

(*c*) *From Iron, Titanium, Cobalt, Nickel, Manganese, Zinc, Beryllium, and Alkaline Earths: Sodium Carbonate Method.*—The boiling neutral solution (about 50 ml.) is poured into a hot solution of 3 g. of sodium carbonate in 50 ml. of water.[1] The liquid is boiled for 10 minutes, diluted to 350 ml., and again boiled for half an hour. The precipitate is allowed to settle, filtered off, washed with 1 per cent. sodium carbonate solution, dissolved in hydrochloric acid, and the whole treatment repeated. The combined filtrate is acidified with hydrochloric acid, boiled till free from carbon dioxide, and the uranium precipitated with ammonia. The precipitate may contain phosphoric acid and small amounts of alumina.

(*d*) *From Iron, Nickel, Cobalt, and Zinc: Sulphide Precipitation from Tartrate Solution.*—The acid solution, containing 3 to 4 g. each of tartaric acid and ammonium chloride, is warmed and treated with hydrogen sulphide until the iron is reduced, made ammoniacal, and treated with 5 ml. of freshly made ammonium sulphide. The precipitate is left to settle overnight, collected, and washed with water containing ammonium chloride and sulphide. The filtrate containing the uranium is acidified with acetic acid, boiled till free from hydrogen sulphide, and precipitated with tannin (§ IV, *b*, 2).

(*e*) *From Iron, Vanadium, Titanium, and Zirconium: Cupferron Method.*—The cold sulphate solution (200 ml.), containing 10 per cent. by volume of sulphuric acid, is treated with a slight excess of permanganate,[2] and then with a decided excess of a freshly prepared, filtered, 6 per cent. solution of cupferron. The precipitate, containing the iron, vanadium, titanium, and zirconium, is mixed with filter-pulp, collected under gentle suction, and washed with 10 per cent. hydrochloric or sulphuric acid. The filtrate is boiled down to 50 ml., treated with 20 ml. of nitric acid, and evaporated until the greater part of the sulphuric acid is expelled. After dilution and filtration, the solution is neutralized with sodium carbonate and treated as under (*c*), *above*.

The separation of sexivalent uranium from the above elements is quantitative in one operation.

(*f*) *From Aluminium, Chromium, Manganese, and Phosphoric Acid: Cupferron-Reduction Method.*[3]—In this operation, the uranium is first reduced to the quadrivalent condition, in which it is quantitatively precipitated by cupferron.

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[1] Hillebrand and Lundell (*op. cit.*, p. 366) recommend addition of sodium peroxide to the carbonate solution.

[2] Hillebrand and Lundell, *op. cit.*, p. 110.

[3] J. A. Holladay and T. R. Cunningham, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 329.

The sulphate solution should be free from nitric acid; if it contains cupferron from the preceding operation (*e*), it is boiled down, treated with nitric acid, and evaporated until the sulphuric acid fumes strongly. The cold acid is diluted with water and the evaporation to strong fumes repeated. The acidity is adjusted to about 6 ml. of sulphuric acid per 100 ml., and the cold solution passed through a Jones reductor, followed by 8 per cent. sulphuric acid. The cold solution is precipitated with excess of cupferron, the precipitate mixed with filter-pulp, collected under slight suction, washed with a solution containing 4 per cent. of sulphuric acid and 0·15 per cent. of cupferron, and ignited to $U_3O_8$.

Bivalent chromium produced by the reduction is partly precipitated by cupferron; this interference can be largely if not completely overcome by exposure of the solution to the air until the chromous salt has re-oxidized.[1]

(*g*) *Uranous from Uranic Uranium.*—(1) *Cupferron method.* From what has been stated under (*e*) and (*f*), *above*, it follows that a separation of quadrivalent from sexivalent uranium can be accomplished by means of cupferron. The cold, acid sulphate solution is precipitated with cupferron, the precipitate thus obtained being ignited to $U_3O_8$ and calculated to $UO_2$. The filtrate from the cupferron precipitate is boiled down, oxidized with nitric acid, evaporated with sulphuric acid, and treated by the cupferron-reduction method as under (*f*); the $U_3O_8$ thus obtained is calculated to $UO_3$.

(2) *Hydrofluoric acid method.*[2] When minerals such as titanoniobates of uranium and the rare earths (which contain uranium in the two states of oxidation) are heated with hydrofluoric acid, they are readily decomposed with precipitation of an insoluble fraction consisting of uranous, thorium, and rare-earth fluorides, and solution of the fluorides of titanium, niobium, tantalum, and sexivalent uranium. The acid is evaporated to 5 ml., diluted with 100 ml. of hot water, and the solution filtered. Precipitate and filtrate are heated with sulphuric acid until the whole of the hydrofluoric acid is expelled, and the uranium is determined in the two portions (*h*, *below*).

(*h*) *From Titanium, Niobium, and Tantalum: Tannin Method.*[3]—The bisulphate melt of the mineral or mixed oxides (in the case of *g*, (2), *above*, the soluble fluorides are heated with sulphuric acid and potassium bisulphate until a clear melt is finally obtained) is dissolved in ammonium oxalate solution, approximately neutralized with ammonia, diluted with an equal bulk of saturated ammonium chloride solution, and precipitated with tannin exactly as described under **XIII,** § III, *d.* The tannin precipitate thus obtained consists of the complexes of the earths of Group A, *viz.* tantalic, titanic, and niobic oxides; the filtrate contains the uranium and the other members of Group B (zirconia, alumina, and beryllia). They are recovered from the tannin filtrate by one of the alternative procedures described under **XIV,** § III, *c*, 1; the ignited product from this operation is fused with bisulphate, and the zirconium, if present, precipitated with cupferron; the excess of reagent is destroyed in the filtrate as under (*e*), *above*, and the uranium (aluminium, beryllium) recovered by ammonia precipitation, preferably with addition of a few ml. of 2 per cent. tannin solution.[1] This is added to the hot suspension of the ammonia precipitate, and has the effect of coagulating the precipitate, as well as counteracting the solvent action of a slight excess of ammonia on the precipitated hydroxides. The separation of uranium from aluminium is discussed under (*i*), from aluminium and beryllium under (*j*), *below*.

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[1] Hillebrand and Lundell, *op. cit.*, p. 373.

[2] J. L. Smith, *Amer. Chem. J.*, 1883, **5**, 73.

[3] W. R. Schoeller and H. W. Webb, *Analyst*, 1933, **58**, 143.

(*i*) *From Aluminium*.—This separation is an important problem of uranium analysis. In the two methods based upon the formation of a soluble complex uranium carbonate (*b* and *c*, *above*), it was noted that the soluble uranium fraction includes a little aluminium. At the same time these procedures are the most commonly employed in ore analysis, ammonium carbonate being the more usual reagent for separations involving aluminium.

(1) L. Moser[2] prescribes neutralization of the solution with ammonia, treatment with a two- to threefold excess of 2N. ammonium carbonate solution, and warming. The aluminium precipitate is collected and washed with hot water containing ammonium carbonate, dissolved in hydrochloric acid, and the above treatment is repeated.

(2) The senior author[3] has proposed treatment of the solid salts with ammonium carbonate solution, which yields a dense precipitate of aluminium hydroxide. The solution of the bisulphate melt of the mixed oxides is neutralized with ammonia and evaporated practically to dryness on a water-bath. The residue is treated with a small excess of freshly made 10 per cent. ammonium carbonate solution, and broken up with a glass rod. Sufficient warm water is added to dissolve the sulphates, and the precipitate allowed to settle, collected on a small filter containing a little pulp, washed with warm water containing 1 per cent. each of ammonium carbonate and chloride, and ignited to alumina. If not perfectly white, it is fused with bisulphate, and the separation repeated. The filtrate is acidified, boiled till free from carbon dioxide, and the uranium precipitated with ammonia (§ IV, *a*). The procedure may serve as a test for subordinate amounts of aluminium, such as would be present in the uranium fraction from the separations described under (*b*) and (*c*), *above*.

(3) The separation by cupferron (*f*, *above*) gives correct results for uranium, but the determination of aluminium is complicated by the introduction of zinc into the solution.

(4) *Phosphate method*.[4] The ammonia precipitate obtained as under (*c*), *above*, is dissolved in nitric acid, and the uranium and aluminium precipitated as phosphates according to § IV, *c*. The washed precipitate is boiled with dilute nitric acid, and the filtered solution boiled with excess of sodium carbonate. Sufficient ammonium chloride is added to decompose the sodium carbonate, and the liquid set aside for two hours. The precipitated aluminium phosphate is filtered off and washed with very dilute ammonium carbonate solution.

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[1] R. E. Divine, *J. Soc. Chem. Ind.*, 1905, **24**, 11.

[2] *Monatsh.*, 1923, **44**, 77.

[3] Schoeller, *op. cit.*, p. 137.

[4] After H. Brearley, *The Analytical Chemistry of Uranium*, London, 1903.

(*j*) *From Aluminium and Beryllium.*[1]—The solution of the bisulphate melt of the mixed oxides is evaporated to dryness, etc., exactly as under (*i*), 2, *above*. The operation gives a precipitate of alumina containing part of the beryllia, the balance (more than one-half) passing into the filtrate along with the whole of the uranium. The precipitate is reserved, while the filtrate is treated with a very slight excess of hydrochloric acid, boiled till free from carbon dioxide, and treated with potassium ferrocyanide for the separation of uranium from beryllium (**VII,** § III, *h*). The filter containing the uranyl ferrocyanide precipitate is returned to the beaker and dissolved in strong sulphuric acid, which is warmed and treated with small quantities of nitric acid until the carbonaceous matter is destroyed. The acid solution is evaporated, cooled, diluted, treated with tartaric acid, and the iron is precipitated as sulphide (*d*, *above*). The uranium in the filtrate is precipitated with tannin (§ IV, *b*, 2).

The beryllium in the ferrocyanide filtrate is recovered by precipitation with ammonia (**VII,** § IV, *a*) and ignition of the precipitate in a platinum crucible together with the reserved alumina containing the balance of the beryllia. The ignited precipitate is fused with sodium carbonate for the separation of aluminium from beryllium (**VII,** § III, *b*, 3); the residual beryllia is weighed, and the minute amount of ferric oxide contained therein (derived from the ferrocyanide) determined colorimetrically.

(*k*) *From Zirconium.*—The cupferron method (*e*, *above*) is the most reliable separation procedure. If the zirconia is precipitated from the neutralized solution by hydrolysis with thiosulphate (**XIV,** § IV, *b*), uranium is coprecipitated to some extent.

Small quantities of zirconium (*cf. b*, *above*) may be separated from uranium by precipitation as phosphate from acid solution containing hydrogen peroxide (**XIV,** § III, *e*, 1).

(*l*) *From Vanadium.*—Vanadium, which is a constituent of carnotite (*q.v.*, **XVII,** § I, *d*, 7), interferes with the determination of uranium by gravimetric and volumetric methods; it also modifies the behaviour of uranium solutions towards sodium hydroxide by preventing precipitation or rendering it incomplete.

(1) The best separation method consists in precipitating the vanadium in the fully oxidized solution with cupferron, destroying the excess of precipitant in the filtrate, and recovering the uranium by ammonia precipitation (*e*, *above*).

(2) The vanadium in the form of vanadic acid is precipitated as lead vanadate (**XVII,** § III, *d*, 2).

(3) According to A. N. Finn,[2] uranium may be precipitated from ammoniacal solution as phosphate. The acid sulphate solution, containing not more than 0·25 g. of $U_3O_8$, is treated with 0·5 g. of ammonium phosphate, boiled, and made ammoniacal. The uranium is precipitated as uranyl ammonium phosphate, vanadium passing into the filtrate. If much vanadium is present, the precipitate is dissolved in dilute nitric acid, and reprecipitated with ammonia; it should be washed with dilute ammonium sulphate

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[1] Schoeller, *op. cit.*, p. 137.

[2] *J. Amer. Chem. Soc.*, 1906, **28**, 1443.

solution. Hillebrand and Lundell[1] find that, with large quantities of the two elements, the gravimetric uranium results still showed positive errors after double precipitation.

(4) In Scholl's method (§ VIII, *c*, 2), the vanadium is converted into ferric vanadate by a suitable addition of ferric chloride and precipitation with sodium carbonate.

(5) W. W. Scott (§ VIII, *c*, 3) separates the two elements by an extraction process utilizing a mixture of glacial acetic and nitric acids, in which uranic nitrate is soluble, vanadic acid remaining undissolved.

(*m*) *From Phosphoric* (*Arsenic*) *Acid.*[2]—The slightly acid chloride solution is treated with excess of potassium ferrocyanide and saturated with sodium chloride; the brown precipitate of uranyl ferrocyanide is collected, and washed with cold saturated salt solution until the washings are free from ferrocyanide. The moist precipitate is digested in the cold with caustic potash, the potassium uranate filtered off, washed with ammonia and ammonium chloride solution till free from ferrocyanide, and dissolved in dilute hydrochloric acid, any insoluble matter being filtered off and again treated with caustic potash. The combined filtrate is treated according to (*a*) if copper is present; iron is next removed as under (*c*). If much arsenic is present, the above direct precipitation of uranium as ferrocyanide is preferable to removal of arsenic as sulphide.

In this procedure, the solution is saturated with sodium chloride to facilitate filtration of the slimy ferrocyanide precipitate. Schoeller and Webb[3] have found that, after admixture of filter-pulp, the ferrocyanide precipitate is readily filtered off and washed (**VII,** § III, *h; cf. j, above*). They decompose the ferrocyanide precipitate with strong sulphuric acid instead of alkali.

Phosphoric acid may be determined in presence of uranium by the standard molybdate process.

§ **IV. Gravimetric Determination.**—Uranium is usually weighed as the oxide $U_3O_8$, which is obtained by ignition of the ammonia precipitate or the tannin complex. It may also be weighed as uranyl pyrophosphate.

(*a*) *Ammonia Precipitation.*—The gravimetric determination of uranium by this method has been re-investigated by G. E. F. Lundell and H. B. Knowles,[4] who proved the procedure to yield very accurate results. They mix the precipitate with filter-pulp and ignite it in air, which is preferable to reducing it to the dioxide by ignition in hydrogen.[5] The incorporation of filter-pulp has the further great advantage that the yellow ammonium uranate precipitate can be readily filtered off and washed, whereas without pulp it soon clogs the filter.

The acid sulphate, nitrate, or chloride solution, free from carbon dioxide and organic matter as well as from other elements precipitated by ammonia, is treated with ammonium nitrate and a small excess of carbonate-free ammonia, and heated to boiling. The yellow precipitate is mixed with a sufficiency of filter-pulp, allowed to settle, collected on a loose-textured filter, washed with hot 2 per cent. ammonium nitrate solution, ignited wet in a tared porcelain crucible, finally for a short time over a blast-burner, and weighed as $U_3O_8$.

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[1] *Op. cit.*, p. 372.

[2] R. Fresenius and E. Hintz, *Zeitsch. anal. Chem.*, 1895, **34**, 437.

[3] *Analyst*, 1936, **61**, 240.

[4] *J. Amer. Chem. Soc.*, 1925, **47**, 2637.

[5] The most accurate procedure according to H. Brearley (*op. cit.*).

The ignited precipitate should be soluble in hot strong nitric acid. The solution may be tested for silica by evaporation to dryness, and for iron and aluminium by solution of the dry residue in ammonium carbonate solution (§ III, *i*, 2, *above*). Any insoluble residue thus obtained is collected, washed, ignited, weighed, and subtracted from the weight of the $U_3O_8$. The filtrate containing the uranium is, if necessary, tested for vanadium by acidification with sulphuric acid, boiling, cooling, and addition of a drop or two of hydrogen peroxide (**XVII**, § VI).

(*b*) *Tannin Precipitation.*—(1) *From acetate solution.*[1] Uranium is precipitated by tannin as a bulky chocolate-brown complex. Acid solutions must first be neutralized with ammonia. The neutral or feebly acid, boiling solution is treated with 5 g. of ammonium chloride, excess of fresh tannin solution (at least 5 parts of tannin to 1 of uranium), and ammoniacal 10 per cent. ammonium acetate solution till the precipitate flocculates and the liquid clears. The precipitate is mixed with filter-pulp, collected, returned to the beaker with slightly ammoniacal ammonium nitrate solution, stirred up, again collected, ignited wet in a tared porcelain crucible, and weighed as $U_3O_8$. It is then tested for silica, etc. as under (*a*), *above*.

The tannin precipitate is not soluble in ammonium carbonate solution; in fact, the solution of uranyl ammonium carbonate is precipitated by tannin and ammonium chloride. Hence tannin is a safer precipitant than ammonia, more particularly for small amounts of uranium, as it counteracts the solvent effect of any carbonate present in the ammonia. The tannin complex of uranium is soluble in mineral acids and in excess of acetic acid.

(2) *From tartrate solution.*[2] Uranium, like iron, aluminium, chromium, vanadium, and the earths of the Fourth and Fifth Groups of the Periodic System, is quantitatively precipitated by tannin from neutralized tartrate solution in the presence of ammonium acetate and chloride. The precipitation is carried out as described under **XIII**, § IV, *c*. The ignited precipitate is weighed as $U_3O_8$, and tested for purity as under (*a*), *above*.

(3) *From oxalate solution.*[2] Ammonium oxalate prevents the precipitation of uranium by ammonia, hence the oxalic acid introduced in the separation of the rare earths from uranium has to be destroyed prior to the determination of the latter. Alternatively, the boiling oxalate solution may be treated with tannin and a slight excess of ammonia, the uranium being quantitatively precipitated. The precipitate is set aside for 3 hours at room temperature, collected, washed with ammonium nitrate solution, ignited, and weighed. Its weight is usually excessive, due to contamination with silica; it should be tested as under (*a*), *above*.

(*c*) *Precipitation as Uranyl Ammonium Phosphate.*[3]—The determination of uranium as phosphate obviates its separation from phosphoric acid. The acid solution is treated with microcosmic salt equal to at least ten times the weight of uranium present, and heated to boiling; ammonia is added drop by drop till a precipitate begins to form; this is cleared with a few drops of dilute nitric acid, after which 1 g. of sodium thiosulphate is added, and the solution boiled. After addition of 10 ml. of 25 per cent. ammonium acetate solution (*i.e.* more than sufficient to replace the nitric by acetic acid) the solution is boiled for 10 minutes longer. The granular precipitate of uranyl ammonium phosphate and sulphur is ignited in a tared crucible, the greenish residue moistened with nitric acid, dried on the water-bath, and gently ignited. It is weighed as $(UO_2)_2P_2O_7$, which should be of a pure lemon-yellow colour.

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[1] P. N. Das-Gupta, *J. Indian Chem. Soc.*, 1929, **6**, 763.

[2] W. R. Schoeller and H. W. Webb, *Analyst*, 1933, **58**, 143.

[3] H. Brearley, *op. cit.*

§ V. **Volumetric Determination.**—Uranium can be accurately determined[1] by reduction to the quadrivalent state and re-oxidation of the uranous to uranyl salt by means of permanganate:

$$UO_2SO_4 + 2H_2SO_4 + Zn = U(SO_4)_2 + ZnSO_4 + 2H_2O;$$
$$5U(SO_4)_2 + 2KMnO_4 + 2H_2O = 5UO_2SO_4 + 2KHSO_4 + 2MnSO_4 + H_2SO_4.$$

(1) The uranyl sulphate solution, free from nitrate and other reducible metals, containing 5 per cent. of sulphuric acid and less than 1 per cent. of metal, is treated with permanganate solution to a permanent pink tint, cooled to 20° C., and passed through a Jones reductor containing 20-mesh amalgamated zinc (45 cm. column, 1 to 2 per cent. mercury) previously washed with 25 ml. of 5 per cent. sulphuric acid, then 250 ml. of hot water. For the determination, 25 ml. of 5 per cent. sulphuric acid is drawn through by gentle suction, followed by the assay solution at the rate of 50 to 100 ml. per minute, this in turn by more of the dilute acid, and finally water. The liquid in the receiver, which is slightly over-reduced, is poured into a capacious porcelain basin and stirred for 5 minutes, when re-oxidation to the stable quadrivalent state takes place. The solution is titrated with 0·05 to 0·1N. permanganate standardized against sodium oxalate. Conversion factors:

$$Na_2C_2O_4 \text{ to } U_3O_8 : 2{\cdot}0951; \quad Na_2C_2O_4 \text{ to } U : 1{\cdot}7766.$$

During reduction the zinc must always be kept covered with liquid. The solution is usually olive-green immediately after reduction, but on exposure to air it changes to sea-green.

(2) Instead of being passed through a reductor, the solution containing 15 per cent. of sulphuric acid may be treated with 10 g. of granulated zinc[2] or strip aluminium,[3] and the action allowed to proceed vigorously for half an hour, after which the reducing agent is filtered off on cotton-wool, and the filtrate titrated with permanganate.

§ VI. **Colorimetric Determination.**—Das-Gupta[4] utilizes the brown coloration of the tannin complex as the basis of a colorimetric process. The neutral solution, containing the metal at a concentration of about 0·02 g. per litre, is treated with 2 ml. of fresh 1 per cent. tannin, and 3 ml. of 5 per cent.

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[1] G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1925, **47**, 2637.

[2] F. Ibbotson and S. G. Clark, *Chem. News*, 1911, **103**, 146.

[3] E. D. Campbell and C. E. Griffin, *J. Ind. Eng. Chem.*, 1909, **1**, 661.

[4] *Loc. cit.*

sodium acetate, solution. Gallic or resorcylic acid may be used instead of tannin.

§ **VII. Detection in Ores.**—All uranium ores are radioactive and affect a photographic plate (see **II,** *d*).

For the detection by chemical tests, the ore is heated with nitric acid (1 : 1), or fused with bisulphate. The nitrate solution is evaporated to dryness, the residue (or the bisulphate melt) taken up with dilute hydrochloric acid, and the heavy metals precipitated with hydrogen sulphide. The filtrate is oxidized with hydrogen peroxide, and, if vanadium is suspected to be present, ferric chloride equal to about 3 times the amount of vanadium is added.[1] The warm solution is neutralized with small portions of solid sodium carbonate, treated with 1 g. in excess, and heated to about 90° C. for 15 minutes. The uranium remains in the solution, which is filtered, acidified with hydrochloric acid, and boiled for the removal of carbon dioxide, after which the following tests may be applied:

(*a*) Ammonia produces a yellow precipitate, soluble in ammonium carbonate; this solution gives a brown precipitate with tannin and ammonium chloride.

(*b*) Potassium ferrocyanide gives a brown precipitate, which on digestion with caustic alkali is converted into yellow uranate.

(*c*) Reduction with zinc causes the yellow colour to change to deep green.

(*d*) Ammonium phosphate, in presence of excess of acetate, produces a greenish-white precipitate.

(*e*) Addition of ammonia and ammonium sulphide produces a brown precipitate soluble in ammonium carbonate.

(*f*) Caustic soda throws down a yellow to orange precipitate from the acid or sodium-carbonate solution.

§ **VIII. Determination in Ores.**—(*a*) *In Ores Free from Rare Earths: Applicable to Phosphate Ores.*—From 0·5 to 1 g. of ore is boiled with 10 ml. of nitric acid until decomposition is complete, hydrochloric acid also being used if necessary. The solution is evaporated to complete dryness, the residue boiled with 3 ml. of hydrochloric acid and 25 ml. of water, the liquid filtered, and the filtrate saturated with hydrogen sulphide (under pressure if molybdenum or arsenic is present). The precipitate is filtered off, the filtrate freed from hydrogen sulphide by boiling, and the iron oxidized with chlorate. The solution is poured into 50 ml. of 10 per cent. sodium carbonate solution, boiled, removed from the heat, treated with 5 g. of ammonium chloride, and set aside for several hours. The precipitate is filtered off and washed with dilute ammonium carbonate solution; if large, it should be dissolved and reprecipitated. The combined filtrates are boiled for the decomposition of ammonium carbonate, slightly acidified with nitric acid, and the carbon dioxide completely expelled by boiling. Microcosmic salt equal to 10 times the uranium present is now added, and nitric acid drop by drop to dissolve any precipitate, followed by 10 g. of sodium thiosulphate and 25 ml. of acetic acid. After 5 minutes' boiling, 10 ml. of 25 per cent. ammonium acetate solution is added, and the boiling continued for another 10 minutes. The precipitate is allowed to settle, washed thoroughly by decantation, then on the filter with hot water, and ignited wet in a porcelain crucible. The residue is moistened with nitric acid, heated till dry, ignited, and weighed as $(UO_2)_2P_2O_7$.

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[1] C. Scholl, *J. Ind. Eng. Chem.*, 1919, **11**, 842.

(*b*) *In Ores Containing Rare Earths but No Phosphoric Acid.*—Uraninite and oxide and silicate ores decomposed by acids are opened up as under (*a*), *above.* Titanoniobates and the like are fused with bisulphate, the melt being extracted with cold dilute hydrochloric acid, and the extract filtered. Either filtrate is treated with hydrogen sulphide, the precipitate filtered off, and the solution boiled and oxidized with nitric acid. It is then neutralized and treated with an excess of 3 g. of sodium carbonate. After boiling and filtering, the precipitate is dissolved in dilute nitric acid and the solution again boiled with an excess of 3 g. of sodium carbonate. The combined filtrates are acidified with hydrochloric acid, boiled till free from carbon dioxide, and precipitated with ammonia. The precipitate is collected, washed with ammonium nitrate solution, dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue dissolved in 2 ml. of hydrochloric acid (1 : 1) followed by 50 ml. of water. The resultant solution is poured into 50 ml. of 10 per cent. oxalic acid, boiled, set aside overnight, filtered, and the precipitate of rare-earth oxalates washed with cold 1 per cent. oxalic acid. The filtrate is evaporated to dryness, the residue gently ignited, dissolved in nitric acid, and the solution warmed with ammonia in excess and ammonium carbonate. The small precipitate of alumina is filtered off, washed with ammonium carbonate solution, dissolved in nitric acid, and reprecipitated with ammonium carbonate. The combined filtrates are boiled for the destruction of the ammonium carbonate, the precipitated ammonium uranate dissolved in nitric acid, reprecipitated with ammonia, mixed with filter-pulp, collected, washed with ammonium nitrate solution, ignited, and weighed as $U_3O_8$.

(*c*) *In Carnotite.*—(1) *Method of Ledoux and Co.*[1] From 2 to 5 g. of ore, according to the quantity of vanadium, uranium, and iron, is digested cold for fifteen minutes with 10 ml. of strong hydrochloric acid with occasional shaking; 5 ml. of nitric acid is added, and the solution heated to boiling and finally evaporated to dryness. The residue is taken up with 3 ml. of hydrochloric acid and 5 ml. of water, and the solution heated on the steam-bath for five minutes, diluted with 25 ml. of hot water, and filtered. The residue, which may contain vanadium, is washed with warm water, ignited in a platinum dish, treated with 5 ml. of hydrofluoric acid, and evaporated to dryness on the steam-bath, avoiding baking; it is taken up with 3 ml. of hydrochloric acid and again evaporated to dryness. The latter process is repeated once more to ensure complete expulsion of hydrofluoric acid, and the final residue taken up with 5 ml. of 1 : 1 hydrochloric acid, warmed until any red crust has dissolved, and filtered into the main liquid, which is then saturated with hydrogen sulphide to precipitate heavy metals.

The filtrate from the sulphides is boiled free from hydrogen sulphide, oxidized with hydrogen peroxide, concentrated to 100 ml., and neutralized with sodium carbonate. Three g. excess is added, the solution boiled for fifteen to twenty minutes, filtered, the precipitate washed with hot water, redissolved in a minimum of nitric acid, hydrogen peroxide added, and the same excess of sodium carbonate. The solution, after boiling for fifteen minutes, is filtered into that from the first precipitation, and the combined filtrates are evaporated to 200 ml., neutralized with nitric acid, and boiled until carbon dioxide is expelled.

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[1] *Bull.* 212, *U.S. Bureau of Mines*, 1923, p. 225.

The solution is neutralized with ammonia, and 4 ml. of nitric acid for each 100 ml. of solution added, followed by 10 ml. of 20 per cent. lead acetate solution and 25 ml. of 25 per cent. ammonium acetate. The liquid is heated on the steam-bath for one hour, filtered through close-textured paper, the precipitate washed with warm water, and dissolved in a minimum of hot 1 : 5 nitric acid; the solution is neutralized with ammonia, and 3 ml. of nitric acid, 2 ml. of lead acetate, and 15 ml. of ammonium acetate solution are added. The precipitate is filtered off and washed as before; the filtrates are concentrated to 400 ml., 10 ml. of strong sulphuric acid is added, and the lead sulphate filtered off and washed with cold water. The filtrate is neutralized with ammonia, an excess of ammonium sulphide added, and the solution heated on the water-bath till the precipitate settles. It is filtered off, washed slightly with warm water, and dissolved in 1 : 2 nitric acid, which is taken to fumes with 5 ml. of sulphuric acid. The cool mass is taken up with water, the solution boiled, and allowed to cool; the small precipitate of lead sulphate is filtered off and washed with dilute sulphuric acid.

The filtrate is nearly neutralized with ammonia, cooled below 30° C., and treated with an excess of 2 g. of ammonium carbonate; the precipitate is allowed to settle, filtered, and washed with warm water. If large or of a yellowish colour, it is dissolved in dilute sulphuric acid and reprecipitated with ammonium carbonate as before. The united filtrates are boiled with dilute sulphuric acid until all carbon dioxide is expelled, a small excess of ammonia is added to the hot solution, and the resultant yellow precipitate of ammonium uranate is mixed with filter-pulp. It is allowed to settle, filtered off, washed with 2 per cent. ammonium nitrate solution, ignited wet, and weighed as $U_3O_8$. The purity of the precipitate should be tested by solution in nitric acid and reprecipitation with ammonium carbonate to make sure it is free from alumina; it should also be tested with hydrogen peroxide for vanadium.

The vanadium is determined in the lead precipitate after solution in dilute nitric acid, evaporation to fumes with 10 ml. of sulphuric acid, dilution, reduction with sulphur dioxide, and titration with permanganate (see **XVII**, § V, *a*, 1). The iron precipitate from the second sodium-carbonate extraction may contain vanadium. It is ignited in a platinum crucible, fused with sodium carbonate, the melt extracted with hot water, the solution filtered, and the filtrate acidified with sulphuric acid, reduced, and titrated.

(2) *Scholl's rapid method.*[1] A quantity of ore judged to contain about 0·2 g. of uranic oxide is attacked with 1 : 1 nitric acid by prolonged digestion. After dilution to 250 ml., the insoluble is filtered off, and the filtrate treated with ferric chloride equivalent to about 3 times the amount of vanadium present. The solution is slightly warmed, and neutralized with solid sodium

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[1] C. Scholl, *J. Ind. Eng. Chem.*, 1919, **11**, 842.

carbonate, of which 1 g. in excess is finally added, and digested in a covered beaker for 15 minutes at about 90° C. The precipitate is filtered off and washed with hot water; the filtrate is gradually neutralized with nitric acid to incipient precipitation of the uranium, boiled till most of the carbon dioxide is expelled, treated with an excess of sodium hydroxide, and boiled for 15 minutes longer: the uranium is precipitated, while the balance of the vanadium and aluminium not previously precipitated passes into the filtrate. The uranium precipitate is collected, washed, dissolved in nitric acid, and the boiling solution precipitated with ammonia and filter-pulp.

The precipitate is collected, washed, ignited, weighed as $U_3O_8$, and tested for purity as under § IV, *a*.

(3) *Scott's glacial acetic acid method*[1] is based on C. A. Pierlé's observation[2] that uranic oxide is completely soluble in a mixture of glacial acetic and strong nitric acids (100 : 5), in which vanadic oxide and nitrate are more or less insoluble. The finely ground ore (0·5 g. of high-grade carnotite or a larger quantity of poorer ore) is boiled with 20 to 40 ml. of nitric acid (1 : 1). When decomposition is complete, the solution is evaporated to dryness and the residue baked for a few minutes. Twenty-five ml. of reagent (*above*) is added and the solution boiled for 5 minutes, the beaker being closed with a round flask containing cold water, which acts as a condenser. The insoluble is collected in a porous crucible and washed with a minimum of reagent.

The filtrate is evaporated to dryness, the residue baked, gently ignited over a free flame till black, and again extracted as before. The filtered extract is once more taken to dryness, and the residue ignited for the destruction of organic matter. The last residue is dissolved in 10 ml. of nitric acid and 40 ml. of water, the solution approximately neutralized with ammonia, and solid ammonium carbonate (3 g.) added to precipitate the last of the iron and aluminium. After addition of a few ml. of ammonia, the solution is filtered, and the precipitate washed with hot water. The filtrate is acidified with nitric acid, boiled till free from carbon dioxide, and precipitated with ammonia and filter-pulp. The precipitate is ignited to $U_3O_8$, and tested for purity (§ IV, *a*).

(*d*) *Rapid Methods.*—(1) *Gravimetric.* The ore is decomposed as described in (*a*), *above*. The filtrate from the silica is diluted to 100 ml., nearly neutralized with ammonia, treated with 5 g. of ammonium carbonate, heated to boiling, and filtered. The precipitate is dissolved in hydrochloric acid and the solution reprecipitated as before. The combined filtrates are boiled to decompose ammonium carbonate, acidified with hydrochloric acid, treated with hydrogen sulphide and filtered, the filtrate oxidized with hydrogen peroxide, and the uranium precipitated as phosphate (*a*, *above*). In this method vanadium interferes by replacing part of the phosphorus in $(UO_2)_2P_2O_7$.

(2) *Volumetric.*[3] A quantity of ore containing not more than 0·25 g. $U_3O_8$ is dissolved in sulphuric acid (1 : 5) and evaporated finally to fumes. The cool mass is taken up in water, the solution treated with an excess of sodium carbonate, and well boiled; the precipitate is filtered off, washed

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[1] W. W. Scott, *J. Ind. Eng. Chem.*, 1922, **14**, 531.

[2] *Ibid.*, 1920, **12**, 60.

[3] A. N. Finn, *J. Amer. Chem. Soc.*, 1906, **28**, 1443.

with hot water, dissolved in a minimum of sulphuric acid (1 : 5), and the precipitation with sodium carbonate repeated. The combined filtrates are acidified with sulphuric acid; 0·5 g. of ammonium phosphate is added, the solution heated to boiling, and made just alkaline with ammonia. After a few minutes' boiling, the precipitated uranyl ammonium phosphate is filtered off, washed with 2 per cent. ammonium sulphate solution, dissolved in dilute sulphuric acid, and treated with 10 to 15 g. of zinc to give a vigorous reduction for 30 minutes. The solution is then decanted through a plug of absorbent cotton-wool, and the flask and filter well washed with dilute sulphuric acid. The filtrate is titrated with 0·05N. permanganate at a temperature of 60° C. Vanadium, if present, will be found in the filtrate from the phosphate precipitation, and may be estimated by any of the usual methods.

§ **IX. Complete Analysis of Ores.**—(*a*) *Oxides and Silicates.*—Mineral mixtures belonging to this class are likely to be of great complexity: rare earths, zirconium, and selenium may be present, in addition to commoner metals of all the analytical groups. The determination of noble and other gases found in most radioactive ores is described *below.*

(1) *First portion: metallic elements and fixed constituents.* One g. of finely crushed ore is decomposed as described under § VIII, *a*.

(α) *Insoluble fraction.* The solution is evaporated to complete dryness, and the residue taken up with dilute hydrochloric acid. The insoluble matter is collected, washed, and extracted with hot ammonium acetate solution; the filtered extract is tested for lead with ammonium sulphide, any precipitate obtained being reserved and added to the main lead fraction. The extracted residue consists of silica, silicates, and possibly barium sulphate (**IV**, Procedure 12). The filtrate from the silica obtained by that procedure is added to the main filtrate (β).

(β) *Hydrogen-sulphide group.* The filtrate from the insoluble fraction is saturated with hydrogen sulphide, the filtrate being tested for complete precipitation of arsenic by renewed treatment with hydrogen sulphide. The precipitate is extracted with sodium sulphide; the extract, which may contain arsenic, antimony, and selenium, is precipitated with acetic acid, the precipitate dissolved in hydrochloric acid and potassium chlorate, the chlorine expelled by evaporation, and the solution saturated with sulphur dioxide. Any selenium is filtered off and rejected, and the filtrate analysed for arsenic and antimony. The sulphides insoluble in sodium sulphide contain copper, lead, bismuth, and possibly selenium. The latter is expelled by evaporation with sulphuric and hydrochloric acids (**XIX**, § III, *b*, 1, α), and the residual solution analysed by the usual methods, any lead found in the insoluble fraction (α) being added to that obtained in the hydrogen-sulphide group.

(γ) *Ammonium-sulphide treatment.* The filtrate from (β) is boiled with nitric acid, treated with 5 g. of ammonium chloride, excess of ammonia, and hydrogen sulphide. The precipitate is allowed to settle, collected, dissolved in hydrochloric acid (and bromine, if necessary), and reprecipitated. The combined filtrates are acidified, boiled down, tested for barium with ammonium sulphate, and then analysed for lime and magnesia.

The ammonium-sulphide precipitate is dissolved in *aqua regia*, and the solution precipitated with a slight excess of ammonia (double treatment). The combined filtrate from this treatment is analysed for manganese, zinc, nickel, and cobalt (**IV**, Procedure 6).

(δ) *The ammonia precipitate* is dissolved in hydrochloric acid, the solution evaporated to dryness, the residue dissolved in 2 ml. of hydrochloric acid (1 : 1) and 50 ml. of water, and the thoria and rare earths precipitated with oxalic acid (§ VIII, *b*). For the analysis of the oxalate precipitate, see **XII,** § III, *b* to *d*.

The filtrate from the oxalate precipitate is heated with sulphuric acid for the destruction of oxalic acid, the acid partly expelled by evaporation, and the solution cooled, diluted, neutralized with sodium carbonate, and treated with 3 g. in excess. The alkaline solution is boiled, diluted to 200 ml., boiled again, and filtered.

The precipitate produced by sodium carbonate may contain iron, aluminium, zirconium, as well as a little nickel and cobalt carried down in the above ammonia precipitation. It is dissolved in dilute hydrochloric acid, and the iron, nickel, and cobalt are precipitated as sulphides after addition of tartaric acid. The filtrate from the sulphides is reserved ($F^4$).

(ε) *Uranium fraction.* The sodium-carbonate filtrate from (δ) contains the uranium, with minor amounts of aluminium and zirconium. It is acidified with nitric acid, boiled free from carbon dioxide, precipitated with ammonia and filter-pulp, and the precipitate ignited and weighed as impure $U_3O_8$. This is next dissolved in nitric acid, the solution evaporated to dryness, and the residue dissolved in ammonium carbonate solution. The small residue (if any) is collected, washed, and ignited. The uranium filtrate is acidified with sulphuric acid, boiled, cooled, and tested for zirconium with cupferron. The sum of the ammonium-carbonate and cupferron precipitates, subtracted from the crude uranium oxide, gives the net weight of $U_3O_8$.

The two small precipitates are fused with bisulphate, and the solution of the melt added to $F^4$, which now contains the whole of the aluminium, titanium, and zirconium. They are separated by cupferron (**XIII,** § III, *e*), the ignited precipitate being weighed as $ZrO_2 + TiO_2$, and tested colorimetrically for titania (**XIII,** § VI).

(2) *Second portion: selenium.* The powdered ore (2 to 5 g.) is attacked with nitric acid, which is evaporated on a covered water-bath. The residue is taken up with hydrochloric acid (1 : 1), the liquid filtered, and the residue washed with the same acid. The filtrate is saturated with sulphur dioxide (**XIX,** § III, *e*).

(3) *Third portion: gases (helium, argon, nitrogen, hydrogen). Hillebrand's method.*[1] One to two g. of ore is mixed with six times its weight of fusion mixture in a platinum boat. The latter is completely surrounded by platinum foil to prevent spattering on to the walls of the porcelain tube, in which the fusion is carried out in a current of pure carbon dioxide. The latter must contain no gases unabsorbed by strong caustic potash solution. When the air in the apparatus has been completely displaced by carbon

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[1] W. F. Hillebrand, *Bull.* 78, *U.S. Geol. Surv.*, 1890, p. 43.

dioxide the tube is heated gently, then to a bright red heat, and kept at that temperature until the volume of gas collected over strong caustic potash in a nitrometer ceases to increase (two to three hours). The gases are transferred to a tube filled with distilled water, and the corrected volume ascertained in the usual manner. To convert the number of millilitres of gases per gram of ore into per cent. by weight, it is necessary to determine the specific gravity of the mixture by weighing the dried gases in a small gas-pipette of known capacity.

(4) *Separate portions* are analysed for water (direct determination), carbon dioxide, sulphur, and sulphur trioxide (**IV**, § VIII, 3).

(*b*) *Titanoniobates.*—The complete analysis of the rare titanoniobate minerals, which is only of mineralogical interest, is beyond the scope of this book. A detailed discussion may be found in the monograph by the senior author.[1]

(*c*) *Phosphates* (*Arsenates*).—(1) *First portion.* One g. of mineral is dissolved in hydrochloric acid, with the addition of nitric acid. After evaporation to dryness, the residue is taken up with hydrochloric acid, and the analysis conducted in the same manner as that of oxide ores up to the end of stage *β* (*a*, 1, *above*). The filtrate from the hydrogen-sulphide precipitate is boiled with nitric acid, neutralized with solid sodium carbonate, and boiled with a further 3 g. of the salt. The precipitate is collected, dissolved in hydrochloric acid, and the precipitation repeated. The combined filtrates contain uranium phosphate with probably a slight admixture of aluminium; the uranium is precipitated as under § IV, *c*, and the weighed precipitate is tested for aluminium as described in § III, *i*, 4.

The precipitate produced by sodium carbonate, consisting of phosphates and carbonates of iron, aluminium, calcium, and barium, is dissolved in hydrochloric acid, and the alkaline earths are separated from phosphoric acid and the sesquioxides by the basic-acetate process. The complete precipitation of the phosphoric acid by this method may require more ferric salt than is present in the solution,[2] in which case the iron content of the mineral will have to be determined in a separate portion.

(2) *Second portion: phosphoric acid.* The mineral is dissolved as described under (1), *above*. The dry residue is dissolved in dilute hydrochloric acid, and the solution treated exhaustively with hydrogen sulphide to precipitate the whole of the arsenic. The filtrate is evaporated to dryness with nitric acid, and the nitric-acid solution of the residue treated by the molybdate process as usual.

(3) *Third portion: combined water.* By Penfield's method.

(*d*) *Carnotite.*—(1) *First portion.* One g. of mineral is treated as a phosphate ore (*c*, 1, *above*) to the point where the solution freed from the hydrogen-sulphide precipitate has been boiled with sodium carbonate.

The precipitate produced by sodium carbonate is ignited, and fused with sodium carbonate in a platinum crucible, the cake extracted with water, and the liquid filtered. The insoluble portion is analysed for iron, titanium, aluminium (major fraction), and all the alkaline earths.

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[1] Schoeller, *op. cit.*, pp. 64–70 and 77–141.

[2] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 8th edition, 1935, **2**, 399.

The filtrate from the sodium-carbonate melt, containing a little vanadate, is added to the solution produced by boiling with sodium carbonate. The combined solutions are acidified with nitric acid, boiled till free from carbon dioxide, and treated with lead and ammonium acetates; the precipitated lead vanadate is dissolved in nitric acid, and the precipitation repeated; the vanadium in the precipitate is determined volumetrically (§ VIII, *c*, 1).

The filtrate from the lead vanadate is freed from excess of lead as under § VIII, *c*, 1; it contains uranium and a little aluminium, which are separated by the ammonium-carbonate treatment described under the same reference. The aluminium precipitate is ignited to $Al_2O_3$, while the weighed $U_3O_8$ is tested for purity as under § IV, *a*.

(2) *Second portion: alkalis.* By J. L. Smith's method; test for lithium.

(3) *Third portion: combined water.*

(4) *Fourth portion: sulphur, if present.*

## XXIII.—RHENIUM.

§ I. **Minerals.**—Rhenium is one of the rarest elements known, occurring only in minute traces in certain ores, chiefly molybdenite. The richest source of the metal so far found contains only 0·002 per cent. The metal is recovered from the residues obtained in the working-up of complex sulphide ores containing molybdenum, derived from a German source.

§ II. **Properties and Compounds.**—(*a*) The *metal* is obtained as a grey powder resembling tungsten, by the reduction of perrhenates of the alkalis with hydrogen. It has a sp. gr. of 21·2, and melts above 3000° C. The metal dissolves in *aqua regia* and in nitric acid, giving perrhenic acid; like osmium it oxidizes readily on heating in air, giving a volatile oxide, $Re_2O_7$.

(*b*) The *heptoxide*, $Re_2O_7$, is the most characteristic compound of rhenium; it is a white crystalline solid, which melts at 220° C., but sublimes above 150° C. Like the corresponding oxide of manganese it readily forms salts of the type $M^1ReO_4$, which, however, are much more stable than the permanganates. Several lower oxides of rhenium are known, *e.g.* $ReO_3$, $ReO_2$, $Re_2O_3$, but none is of analytical importance.

(*c*) *Rhenium tetrachloride*, $ReCl_4$, forms with chlorides of the alkali metals and ammonium double salts of a type resembling the chlorosmates, *i.e.* $M^I_2ReCl_6$.

(*d*) *Rhenium heptasulphide*, $Re_2S_7$, is a black precipitate obtained by heating chloride solutions of the heptoxide with hydrogen sulphide; it is insoluble in alkali sulphides.

§ III. **Quantitative Separation.**—Rhenium belongs to Group II of the analytical separation scheme, its sulphide being precipitated from acid solutions by the passage of hydrogen sulphide. Chloride solutions containing the heptoxide should not be boiled, as the oxide is appreciably volatile, especially in the absence of alkali chlorides. This behaviour is utilized in the separation of the metal from most metals with which it is associated.

(*a*) *From Metals not Precipitated by Hydrogen Sulphide.*—The acid solution free from nitrate is adjusted to contain 5 per cent. of free hydrochloric acid, and a rapid current of hydrogen sulphide is passed through for at least an hour. Extraction of the washed precipitate with sodium sulphide solution removes most of the molybdenum, arsenic, and antimony, but traces of rhenium are liable to dissolve.

(*b*) *Distillation Process.*[1]—The rhenium solution is treated with 150 ml. of 80 per cent. sulphuric acid and 10 ml. of syrupy phosphoric acid in a distillation flask attached to a condenser and an ice-cooled receiver. A flask containing 300 ml. of 1 : 1 hydrochloric acid is connected to the distillation flask by a tube passing below the liquid level in the latter. A current of carbon dioxide is passed through the whole apparatus for some time, the distillation flask is heated to 160° C., and then the hydrochloric acid is gently boiled; the carbon dioxide drives the vapour of the latter acid through the sulphuric-acid solution, causing the rhenium to distil over into the receiver. The operation is continued until 200 ml. of hydrochloric acid has been distilled through the apparatus. The rhenium in the distillate is recovered by adjusting the acidity to 5 to 10 per cent. by addition of ammonia and saturation of the solution with hydrogen sulphide.

(*c*) *From Molybdenum: 8-Hydroxyquinoline Method.*—The alkaline solution, obtained for example by fusion of the material with sodium peroxide, is treated with an excess of 5 ml. of N. sulphuric acid, and 5 ml. of 2N. sodium acetate solution, and the molybdenum is precipitated by adding a 5 per cent. solution of 8-hydroxyquinoline to the boiling solution until no further precipitate forms (**XX,** § IV, *b*). This is filtered off and washed with hot water, and the filtrate acidified with hydrochloric acid (to 5 per cent. of free acid) and saturated with hydrogen sulphide for the recovery of the rhenium.

§ **IV. Gravimetric Determination.**—(*a*) *With Nitron Acetate.*[2]—The sulphide precipitate obtained as described in § III is digested with 5 per cent. sodium hydroxide solution, and 30 per cent. hydrogen peroxide is added drop by drop until a colourless solution is obtained. The solution is evaporated to 40 to 50 ml., acidified with dilute sulphuric acid, and filtered. The filtrate is heated to 60° C., and the rhenium precipitated by adding 5 per cent. nitron acetate solution; after cooling to 0° C. the precipitate of nitron perrhenate is collected in a Gooch or porous glass crucible, washed first with an ice-cold 0·3 per cent. solution of nitron acetate and then with 1 to 2 ml. of ice-cold water, dried at 105° C. for an hour, and weighed as $C_{20}H_{16}N_4HReO_4$, which contains 33·06 per cent. of rhenium.

(*b*) *With Tetraphenylarsonium Chloride.*[3]—The perrhenate solution, free from nitrate and molybdate and not exceeding 60 ml. in volume, is treated with 3 to 4 g. of sodium chloride and, after heating to 60° C., with a small excess of a 5 per cent. solution of tetraphenylarsonium chloride. The mixture is well stirred to cause the precipitate to crystallize, cooled to 0° C., and filtered through a glass crucible. The precipitate is washed with ice-water, dried at 110° C., and weighed as $(C_6H_5)_4AsReO_4$, which contains 29·40 per cent. of rhenium.

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[1] W. Geilmann and F. Weibke, *Zeitsch. anorg. Chem.*, 1931, **199**, 120.

[2] W. Geilmann and A. Voigt, *ibid.*, 1930, **193**, 311; W. Geilmann and F. Weibke, *ibid.*, 1931, **195**, 289.

[3] H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 305.

§ V. **Volumetric Determination.**[1]—If a 5 per cent. sulphuric acid solution containing perrhenic acid is electrolysed at 70° C. for 3 hours with 2·3 to 2·5 volts, the rhenium is quantitatively deposited as a mixture of metal and oxide on the cathode. The deposit is dissolved in 10 per cent. hydrogen peroxide solution, the excess of the latter destroyed by boiling, and the perrhenic acid determined by titration with 0·01N. sodium hydroxide (methyl red as indicator).

§ **VI. Detection in Ores.**—No reliable method for the detection of the metal in ores has yet been worked out. Probably the best procedure consists in dissolving the ore in *aqua regia* on the water-bath, evaporating with sodium chloride and hydrochloric acid to expel nitric acid, and saturating the solution with hydrogen sulphide. The sulphide precipitate is dissolved in alkaline hydrogen peroxide, and the solution distilled as described in § III, *b* to recover the rhenium. The distillate is treated with hydrogen sulphide, and the rhenium sulphide dissolved in alkaline hydrogen peroxide. The solution is filtered and evaporated to a small volume; addition of a drop of dilute permanganate and a few drops of cæsium chloride solution produces a pink crystalline precipitate of cæsium perrhenate (coloured with permanganate), isomorphous with cæsium perchlorate; the crystals consist of small, highly refracting bipyramids.

Rhenium may also be detected by examining the spark spectrum of the sulphide precipitate remaining after extraction with sodium sulphide for the lines 3451·28, 3460·47 and 3463·72A.

§ **VII. Determination in Ores.**—Since only minute traces of rhenium have so far been found in any ore, no satisfactory method for the determination of the metal in ores has yet been worked out. The best procedure would seem to be to concentrate the rhenium from a large weight of ore, *e.g.* 50 to 100 g., in a sulphide precipitate as described in § VI, and then to dissolve this precipitate in alkaline hydrogen peroxide and distil the rhenium as described in § III, *b*; the distillate is analysed by the oxine-sulphide-nitron methods (§ III, *b* and *c*; § IV, *a*).

## XXIV.—THE PLATINUM METALS.

§ **I. Minerals.**—(*a*) *Native Metals and Alloys.*—(1) *Platinum* is found native, in the form of an alloy containing usually 75 to 85 per cent. of platinum, the balance consisting chiefly of iron and smaller quantities of iridium, palladium, rhodium, copper, and nickel. It is found in alluvial deposits (resulting from the disintegration of basic igneous rocks such as peridotite, norite, gabbro, and their alteration product, serpentine) in whitish to steel-grey, flattened grains or pellets, or nuggets (stained brown or black) of irregular shape, of sp. gr. 16 to 19; H. 4 to 4·5. The alluvial deposits or gravels consist mainly of chromite, magnetite, ilmenite, spinel, corundum, zircon, and quartz; besides platinum, they usually carry osmiridium (2, *below*) and gold. The precious minerals are found in the deposits in minute proportions (a few grams per ton). Native platinum is malleable and ductile, often ferromagnetic, and soluble in *aqua regia* (distinction from osmiridium).

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[1] O. and F. Tomíček, *Trans. Electrochem. Soc.*, 1939, Preprint 16.

(2) *Osmiridium* (*iridosmine*) is a native alloy, the principal constituents of which are iridium and osmium. Two varieties of osmiridium are recognized: in *nevjanskite*, iridium preponderates over osmium, while if the reverse is the case the mineral is termed *siserskite.* The two main constituents usually account for 70 to 90 per cent. of the mineral; the balance is made up of ruthenium, platinum, rhodium, and small quantities of iron and copper, but palladium does not occur in osmiridium. It is found in hard flattened grains or pellets, sometimes in hexagonal prisms, of white or grey colour. H. 6 to 7; sp. gr. 19 to 21. It is hard and brittle, non-magnetic, and insoluble in *aqua regia.* When heated to redness, the osmium-rich varieties give off osmium tetroxide, recognizable by its pungent odour. It occurs in alluvial deposits with native platinum (1, *above*). Occasionally native gold is accompanied by osmiridium: thus the banket gold ore of the Witwatersrand contains minute amounts (of the order of 1 oz. per 10,000 tons [1]); yet, on account of the huge tonnage treated, it constitutes one of the most important sources of osmiridium. Several thousand ounces per year are recovered, the mineral accumulating during the fine grinding of the ore in the cyanide process. The osmiridium occurs in minute grains (mostly finer than 200-mesh), in which the average Os : Ir : Ru : Pt ratio works out at about 3 : 3 : 1 : 0·5. The mineral also occurs independently, as in Tasmania (approximate Os : Ir : Ru : Pt ratio, 3 : 3 : 0·5 : 0·1).

(3) *Platiniridium*, an alloy consisting mainly of iridium and platinum in varying proportions; either may predominate. White metallic pellets, insoluble in *aqua regia*, associated with native platinum. H. 6 to 7; sp. gr. 22.

(4) *Palladium* has been found substantially pure in the form of grains, accompanying native platinum.

(5) *Native gold* from some South American localities contains several per cent. of palladium besides silver; another occurrence is characterized by a small rhodium content.

(*b*) *Sulphides, Arsenides, and Antimonides.*—(1) *Laurite*, ruthenium sulphide, probably $RuS_2$, is a very rare, iron-black, cubic mineral containing also a little osmium. H. 7·5; sp. gr. 7·0.

(2) *Sperrylite*, platinum diarsenide, $PtAs_2$, is tin-white with a metallic lustre. Cubic; large crystals have been found. Brittle; H. 6 to 7; sp. gr. 10·6. Contains a little rhodium and antimony. Insoluble in *aqua regia*, but soluble after roasting.

(3) *Cooperite*, platinous sulphide, PtS, is a steel-grey, brittle, cubic mineral of metallic lustre. Insoluble in *aqua regia*, but roasting converts it into spongy platinum; does not tarnish when heated.

(4) *Braggite*, platinum palladium nickel sulphide, (Pt, Pd, Ni)S, resembles cooperite but gives " temper colours " when gently heated in air, and a black residue of oxides after roasting. Attacked by molten potassium bisulphate, giving a red-brown melt and a residue of spongy platinum.

(5) *Stibiopalladinite*, palladium antimonide, $Pd_3Sb$, is a brittle, grey mineral of metallic lustre, soluble in *aqua regia.*

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[1] J. R. Thurlow, *J. Chem. Met. Min. Soc. S. Africa*, 1922, **22**, 209.

The above five minerals, the last three of which have been discovered fairly recently, occur in the platiniferous copper nickel sulphide ores of the Transvaal. Sperrylite was first identified in the nickel-copper ore deposit of Sudbury, Ontario.

(*c*) *Base-metal Ores.*—Minute quantities of platinum metals, chiefly platinum and palladium, occur in many sulphide ores of the base metals, such as copper ores. Whilst these small traces usually escape detection in routine assaying for gold and silver, the platinum metals become concentrated in the electrolytic refinery sludge after accompanying the copper in the smelting processes.

**§ II. Properties and Compounds.** — The time-honoured term "platinum metals" conveniently embraces the six elements originally isolated from alluvial deposits containing native platinum and osmiridium. They are placed in Group VIII of the Periodic System, being subdivided into two triads, *viz.* the lighter platinum metals (Ruthenium Group) and the heavier platinum metals (Osmium Group). Again, they may be grouped in three pairs according to their vertical order in the Periodic System, the members of each pair having certain properties in common:

Ruthenium Group: Ru . . . Rh . . . Pd
Osmium Group: Os . . . Ir . . . Pt

(*a*) The *elements* have the following densities and melting-points:

| | Ru. | Rh. | Pd. | Os. | Ir. | Pt. |
|---|---|---|---|---|---|---|
| Sp. gr. | 12·26 | 12·4 | 11·9 | 22·48 | 22·5 | 21·4 |
| M.p. (°C.) | > 2500 | 1966 | 1554·4 | > 2500 | 2454 | 1773·5 |

The compact metals are white to greyish-white, except osmium, which has a bluish lustre; the precipitated metals form deep black, heavy powders which exhibit powerful catalytic activity. Only palladium and platinum are soluble in *aqua regia*, although the other metals when finely divided are more or less attacked unless they have been strongly heated.

Whilst the six metals resemble one another more or less in some respects, osmium and palladium exhibit the greatest dissimilarity in their chemical properties. For a comparative study of their analytically important compounds, the following serial arrangement is of advantage, as it brings out a gradual transition in chemical deportment:

| Metal. | Sodium Salts. | Volatile Oxides. | Chlorides. |
|---|---|---|---|
| **(1) Osmium** . | $Na_2OsO_4$ | $OsO_4$ | ($OsCl_4$) |
| **(2) Ruthenium** . | $Na_2RuO_4$ | $RuO_4$ | $RuCl_3$ |
| **(3) Rhodium** . | | | $RhCl_3$ |
| **(4) Iridium** . | | | $IrCl_3$; $IrCl_4$ |
| **(5) Platinum** . | | | $PtCl_4$; $PtCl_2$ |
| **(6) Palladium** . | | | $PdCl_4$; $PdCl_2$ |

This order will be adhered to in the brief list of compounds given *below*, only those of outstanding practical importance to the analyst being described.

(*b*) *Oxides and their Derivatives.*—In this class of compounds the tetroxides of osmium and ruthenium are of outstanding importance, since they place these two elements apart from their congeners. The trioxides of the two elements form soluble alkali salts (osmates and ruthenates). The hydroxides of quadrivalent osmium and iridium are of great analytical interest. Ruthenium and rhodium form hydrated sesquioxides. The oxides of platinum and palladium are analytically unimportant; hydrated palladium dioxide is precipitated by bromate hydrolysis.

(1) *Osmium.* (α) The *tetroxide*, $OsO_4$, is the most important and characteristic osmium compound. It forms colourless, transparent needles which melt at about 40° C. and begin to sublime at a slightly higher temperature; the liquid boils at 134° C., giving a colourless vapour. This has a most penetrating odour recalling that of chlorine or ozone, and acts as a violent poison on the mucous membranes of the lungs, etc.; it is reduced in contact with the tissues, and produces most serious injury to the eyesight. The crystals stain the skin black and cause painful sores. The tetroxide is formed when the metal is heated in air or oxygen, when a soluble osmium compound or finely divided osmium is heated with nitric acid or *aqua regia*, or by distillation of osmate solutions with chlorine, bromine, or alkali chlorate or bromate; in all cases the tetroxide is evolved in the state of vapour. It is soluble in water to a colourless liquid devoid of acid reaction ("perosmic" acid does not exist) and emitting the characteristic smell of the compound. The lower oxide, $OsO_2$, is not volatile.

(β) *Sodium osmate*, $Na_2OsO_4$, is obtained when solid or gaseous osmium tetroxide acts on sodium hydroxide in the presence of a reducing agent (*e.g.* alcohol), the solution assuming a deep purple colour. The reddish-violet potassium salt may be prepared in the same manner, or by precipitation of sodium osmate solution with strong caustic potash.

(γ) *Hydrated osmium dioxide*, $OsO_2.2H_2O$, is obtained as a deep black, pulverulent precipitate when a solution of alkali osmate containing alcohol is decomposed with the required amount of acid:

$$Na_2OsO_4 + C_2H_5OH + H_2SO_4 = OsO_2.2H_2O + Na_2SO_4 + CH_3CHO.$$

When heated in the air, it is converted into volatile tetroxide; hydrogen or coal-gas at a moderate heat reduces it to the metal.

(2) *Ruthenium.* (α) The *tetroxide*, $RuO_4$, is the characteristic ruthenium compound, though less readily formed and more unstable than the corresponding oxide of osmium. Ruthenium tetroxide is a yellow solid which melts at 25·5° C. and sublimes at higher temperature, decomposing at 107° C. with a smoky flame, forming the dioxide; the vapour is explosive, poisonous, and of an offensive odour. For its preparation, the solution of alkali ruthenate or other soluble ruthenium compound mixed with excess of caustic alkali is saturated with chlorine in a retort and gently heated, when the tetroxide volatilizes as a yellow vapour and condenses in the form of yellow drops, solidifying to a crystalline mass soluble in water. The solution is unstable and deposits a black precipitate; it readily oxidizes organic

substances. Ruthenium tetroxide is not formed by distillation of ruthenium solutions with nitric acid (*cf.* osmium, 1, $\alpha$, *above*). Hot hydrochloric acid reduces it to ruthenium trichloride (*c*, 2, *below*).

($\beta$) *Sodium ruthenate*, $Na_2RuO_4.2H_2O$, is obtained by fusion of the element or its compounds or minerals with sodium hydroxide and nitrate, chlorate, or peroxide; treatment of the melt with hot water gives a deep orange-red solution of the salt. When this is treated with chlorine, *sodium perruthenate* is formed:

$$2Na_2RuO_4 + Cl_2 = 2NaRuO_4 + 2NaCl,$$

the colour of the solution turning a deep greenish-yellow. Complete saturation of the solution with chlorine converts the perruthenate into ruthenium tetroxide:

$$2NaRuO_4 + Cl_2 = 2RuO_4 + 2NaCl.$$

($\gamma$) *Hydrated ruthenium sesquioxide*, $Ru_2O_3.3H_2O$, is a black precipitate resulting from the action of alkali hydroxide, carbonate, or bicarbonate on solutions of the trichloride.

(3) *Rhodium*. The *hydrated sesquioxide* is, like the corresponding ruthenium compound, obtained by double decomposition of sodium chlororhodite with alkali bicarbonate, etc. as a yellow to yellowish-brown flocculent precipitate.

(4) *Iridium*. The *hydrated dioxide* is a deep blue precipitate formed by the action of alkali hydroxide or bicarbonate upon a boiling solution of sodium chloriridate, or by bromate hydrolysis.

(*c*) *Chlorides and their Derivatives.*—The most important chlorides have been tabulated under (*a*), *above*. It must be borne in mind, however, that chloride solutions of the platinum metals do not contain the simple chlorides, but complex chloro-acids or their salts. The table *below* shows the water-soluble sodium salts derived from the chlorides given in the preceding table (the chlorine compounds of osmium find little analytical application):

| Metal. | Chloro . . . ites. | Chloro . . . ates. | Chloro . . . ites. |
|---|---|---|---|
| (1) Osmium . | | ($Na_2Os^{IV}Cl_6$) | |
| (2) Ruthenium . | $Na_2Ru^{III}Cl_5$ | | |
| (3) Rhodium . | $Na_3Rh^{III}Cl_6$ | | |
| (4) Iridium . | $Na_3Ir^{III}Cl_6$ | $Na_2Ir^{IV}Cl_6$ | |
| (5) Platinum . | | $Na_2Pt^{IV}Cl_6$ | $Na_2Pt^{II}Cl_4$ |
| (6) Palladium . | | $Na_2Pd^{IV}Cl_6$ | $Na_2Pd^{II}Cl_4$ |

(2) *Ruthenium*. The *trichloride* is obtained when a solution of the tetroxide in moderately strong hydrochloric acid is boiled, the yellow solution turning a deep brownish-red (distinction from osmium):

$$2RuO_4 + 16HCl = 2RuCl_3 + 8H_2O + 5Cl_2.$$

The neutral solution hydrolyses when warmed, with the formation of a deep black precipitate of the oxychloride. When the acid solution is evaporated with excess of ammonium chloride, a brown crystalline precipitate of *ammonium chlororuthenite*, $(NH_4)_2RuCl_5$, is obtained. The compound is slightly soluble in strong ammonium chloride solution, the supernatant liquid being coloured a light brown.

(3) *Rhodium.* The *trichloride* may be prepared from the finely divided metal by the action of chlorine at a dull red heat. It is a red powder insoluble in water or acids. If a mixture of finely divided rhodium and the required quantity of sodium chloride is strongly heated in a current of chlorine, *sodium chlororhodite*, $Na_3RhCl_6$, is obtained as a deep red melt, which is soluble in water, the solution containing the hydrate $Na_3RhCl_6.9H_2O$. The sodium salt is insoluble in alcohol (distinction from the other sodium chloro-salts here described, with the exception of the chloriridite). *Ammonium chlororhodite*, $2(NH_4)_3RhCl_6.3H_2O$, is soluble in water, but less so in ammonium chloride solution, from which it crystallizes in needles. When a chlororhodite solution is treated with excess of ammonia and concentrated by evaporation, it deposits pale yellow crystals of *chloropentamminerhodium dichloride*, $[RhCl(NH_3)_5]Cl_2$ (*Claus's salt*), which is very stable, but is reduced to metal by zinc. The ammine compounds of rhodium closely resemble those of cobalt.

(4) *Iridium. Sodium chloriridate*, $Na_2IrCl_6$, is formed when a mixture of sodium chloride and iridium powder is heated to a dull red in chlorine. It is very soluble in water and in alcohol. It may be obtained also by solution of the hydroxide or sulphide in *aqua regia* and evaporation with sodium chloride. The reddish-black crystals of $Na_2IrCl_6.6H_2O$ form a deep brown solution, from which ammonium or potassium chloride precipitates crystalline reddish-black *ammonium* or *potassium chloriridate*, $(NH_4)_2IrCl_6$ or $K_2IrCl_6$, insoluble in excess of the precipitant. The above salts are analogous to and isomorphous with the corresponding chloroplatinates, but are readily reduced to *chloriridites*, $M^I{}_3IrCl_6$, by ferrous salts, oxalic acid, stannous chloride, sulphur dioxide, hydroxylamine, hydrazine, etc. *Sodium chloriridite*, $Na_3IrCl_6.12H_2O$, forms dark olive-green crystals soluble in water but insoluble in alcohol (*cf.* 3, *above*). The olive-green ammonium and potassium salts are likewise soluble in water. *Aqua regia* oxidizes the chloriridites to chloriridates.

(5) *Platinum* is soluble in *aqua regia*, the resultant solution containing *chloroplatinic acid*, $H_2PtCl_6.6H_2O$ (reddish deliquescent crystals very soluble in water and in alcohol), and *nitrosyl chloroplatinate*, $(NO)_2PtCl_6$ (brownish-yellow deliquescent crystals decomposed by hydrochloric acid). Repeated evaporation of the mixed solution with hydrochloric acid to the consistency of a syrup yields a solution of pure chloroplatinic acid. With the respective alkali chlorides, the acid gives *sodium chloroplatinate*, $Na_2PtCl_6.6H_2O$, red triclinic prisms very soluble in water and in alcohol; *ammonium chloroplatinate*, $(NH_4)_2PtCl_6$, yellow octahedra sparingly soluble in cold water (0·66 part in 100 of water) and insoluble in strong ammonium chloride solution; and *potassium chloroplatinate*, $K_2PtCl_6$, indistinguishable from the preceding (0·9 part dissolve in 100 of cold water); when ignited, the ammonium salt leaves a residue of spongy platinum, while the potassium salt yields a mixture of potassium chloride and platinum. The anhydrous

sodium salt may be obtained by treatment of a mixture of sodium chloride and platinum with chlorine at a red heat.

Reduction of chloroplatinate solutions (*e.g.* with stannous chloride or sulphur dioxide) produces water-soluble, red *chloroplatinites*, $M^{I}_2PtCl_4$.

(6) *Palladium. Chloropalladic acid*, $H_2PdCl_6$, forms a deep red unstable solution when the metal is dissolved in *aqua regia*; upon evaporation it is converted into reddish-brown *palladous chloride*, $PdCl_2.2H_2O$. The *chloropalladates* of ammonium and of potassium, $(NH_4)_2PdCl_6$ and $K_2PdCl_6$, are bright red crystalline precipitates obtained by evaporation of palladous chloride solutions with alkali chloride and a large excess of nitric acid. Like the corresponding chloriridates and chloroplatinates (*above*), they are insoluble in solutions containing excess of ammonium or potassium chloride. The brown *chloropalladites*, $M^{I}_2PdCl_4$, are soluble in water. When a solution of palladous chloride is made ammoniacal and re-acidified with hydrochloric acid, fine yellow needles of *dichlorodiamminepalladium*, $[Cl_2(NH_3)_2Pd]$, are precipitated.

(*d*) *Sulphides.*—All the platinum metals react with hydrogen sulphide, their acid solutions affording dark brown to black precipitates, mostly of more or less indefinite composition. Qualitatively considered, the precipitates have no distinctive properties leading to the identification of the platinum metals or their separation from other members of the hydrogen-sulphide group. In quantitative analysis, the sulphides of ruthenium and osmium are the most useful (§ IV, 59, 60); as for the other four elements, precipitation by hydrogen sulphide is a procedure of more questionable value, for the reasons given in § III, 14 and § IV, 70.

(*e*) *Complex Nitrites.*—Amongst the innumerable complex derivatives of the platinum metals, the " double " nitrites are of practical interest to the analyst, since the sodium nitrito-salts are very soluble in water and stable in feebly alkaline solution, in which base metals are precipitated as hydroxides or basic salts (§ III, 16). Hence sodium nitrite may be described as a group reagent for the platinum metals. The constitution of the metallonitrites corresponds to that of the sodium chloro . . . ites tabulated under (*c*), *above*:

(2) Ruthenium: $Na_2Ru(NO_2)_5$
(3) Rhodium: $Na_3Rh(NO_2)_6$
(4) Iridium: $Na_3Ir(NO_2)_6$
(5) Platinum: $Na_2Pt(NO_2)_4$
(6) Palladium: $Na_2Pd(NO_2)_4$

The " double " nitrites are formed when hot neutral or feebly acid solutions of the " double " chlorides are treated with excess of sodium nitrite. Generally speaking, the conversion is marked by a bleaching of the solution, the complex nitrites possessing various tints from deep yellow to almost white. When heated with hydrochloric acid, the nitrites are readily decomposed with regeneration of the double chlorides, the iridonitrites and platinonitrites yielding chloriridates and chloroplatinates respectively.

(*f*) *Sulphates.*—Only the sulphates of rhodium and palladium need be mentioned here. Platinum is only very slightly attacked by hot concentrated sulphuric acid or fused bisulphate.

(3) *Rhodium sulphate*, $Rh_2(SO_4)_3$, is obtained by the action of hot strong sulphuric acid on spongy rhodium. The aqueous solution has a deep orange colour, which becomes yellow on dilution. Finely divided rhodium is attacked by fused bisulphate, giving an orange-red melt which contains a double sulphate, $M^I_2SO_4.Rh_2(SO_4)_3$. *Rhodium alums* have been prepared.

(6) *Palladous sulphate*, $PdSO_4.2H_2O$, may be obtained from the metal by heating with strong sulphuric acid, or by fusion with bisulphate. It forms reddish-brown deliquescent crystals soluble in water, yielding an orange to yellow solution.

(*g*) *Miscellaneous Palladium Compounds.*—The only other derivatives of analytical importance to be mentioned here are certain palladium compounds which establish the transitional character of palladium between the platinum metals and silver and the base metals.

*Palladous nitrate*, $Pd(NO_3)_2$, is formed when the metal is dissolved in fuming nitric acid; brownish-yellow, deliquescent crystals. *Palladous iodide*, $PdI_2$, a black flocculent precipitate, is obtained by the addition of hydriodic acid or potassium iodide to palladium solutions. The precipitate is insoluble in hydrochloric acid, but dissolves in excess of potassium iodide, forming a red solution. Unlike platinum, palladium is stained black by iodine. *Palladous cyanide*, $Pd(CN)_2$, is a yellowish-white gelatinous precipitate produced by mercuric or potassium cyanide in palladium solutions. It is very slightly soluble in hydrochloric acid, but readily so in potassium cyanide or ammonia. The other platinum metals are not precipitated by cyanide. *Palladium dimethylglyoxime*, $[(CH_3)_2C_2NOH:NO]_2Pd$, is a bulky orange-yellow precipitate, as characteristic of palladium as is the corresponding red precipitate of nickel. The palladium compound is quantitatively precipitated from 0·25N. hydrochloric- or nitric-acid solutions, while the nickel compound is soluble in dilute mineral acids, its quantitative precipitation necessitating the addition of a slight excess of ammonia or alkali acetate. When ignited, the palladium precipitate leaves a residue of spongy palladium.

§ **III. Quantitative Separation.**—In the past twenty years, all the metals of the platinum group have acquired practical importance. Simultaneously their analytical chemistry and preparation in the pure state have been more thoroughly explored, a task in which the U.S. Bureau of Standards and the Platinum Institute of the U.S.S.R. Academy of Sciences have taken a leading part. The time-honoured processes for the separation of the platinum metals from one another and from certain other elements were in need of thorough revision. As in the case of the earth acids, a clean sweep had to be made of a number of procedures based on selective solution or extraction of complex precipitates. Again, the indiscriminate application of ammonium chloride in separations involving the platinum metals had to be restricted. The investigators of the U.S. Bureau of Standards, rejecting its use altogether, elaborated a procedure [1] for the separation of the six platinum metals in which no ammonium chloride is employed. It must be borne in mind, however, that the scheme deals only with the ideal case of a common solution of the members of the platinum group free from all other metals.

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[1] R. Gilchrist and E. Wichers, *J. Amer. Chem. Soc.*, 1935, **57**, 2565.

The problems encountered in actual practice are far more complex, inasmuch as it is usually impossible to prepare a solution of the very refractory materials under discussion without introducing fluxes or other metals into the solution, not to mention gold, silver, and common elements associated with the platinum metals in their ores, alloys, and metallurgical products.

Having for many years been engaged in analytical and preparative work on the platinum group, we still adhere to the view that " the time has not yet come for the rejection of ammonium chloride as an important reagent in platinum-metals analysis. Ammonia as a precipitant for alumina in rock analysis is by no means an ideal reagent, yet, *faute de mieux*, it has been made to serve the ends of the petrologist. In the same way, ammonium chloride in practised hands is a most serviceable—possibly indispensable—reagent in precious-metal work. Needless to say, the ammonium-chloride precipitate is analysed or retreated, somewhat like the ammonia precipitate in rock analysis." [1]

The objections raised against the precipitation of platinum metals by ammonium chloride are twofold: (i) There is the undisputed fact that the ammonium-chloride precipitate is prone to occlude a fraction of the metals which it is intended to keep in solution. This tendency can be met quite effectively by a repetition of the procedure—a technique to which it would be difficult to object, since double treatment is the rule rather than the exception in analytical work. (ii) The precipitates produced by ammonium chloride are represented as not being sufficiently insoluble for quantitative work unless their solubility is repressed by a suitable excess of precipitant, in which case the objection cited under (i) again operates. As the first objection has already been answered, we submit that the second adds nothing material to the case against ammonium chloride. Summing up, we consider that ammonium chloride merely shares the drawbacks common to a large number of analytical reagents. To cite only one further example, the arguments given *above* can be advanced with the same force against oxalic acid as a reagent for the rare-earth group. At the present time we cannot afford to discard either oxalic acid or ammonium chloride, for the simple reason that no other reagents have yet been found to replace them altogether. Meanwhile, the competent analyst, who has to adapt the known properties of chemical compounds to his purposes, endeavours (not unsuccessfully) to steer a middle course between the dangers of high results by coprecipitation and of low results by incomplete precipitation.

As an illustration of how this can be done we may cite the process of fractional precipitation, based upon the following principle [2]: " If a substance cannot be precipitated quantitatively in one operation without undue contamination, it may be feasible to obtain it in two fractions. The first or major fraction should be pure. The minor fraction completes the precipitation; it is not pure, but, if sufficiently small, renders the error negligible for practical purposes." If not, purification or retreatment of a small fraction is more convenient and effective than that of the whole precipitate.

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[1] W. R. Schoeller, *Analyst*, 1930, **55**, 354.

[2] W. R. Schoeller, *ibid.*, 1930, **55**, 550.

A practical application of the above principle[1] is the determination of platinum in platinum ore by the chlorine process (§ III, 11; § VIII, 91, δ).

The quantitative separation of the platinum metals from other elements and from one another is a much more complex subject than the separation procedures described in the earlier part of this book. To avoid repetition we therefore propose presenting the subject-matter of this section under four broad headings, *viz.*:

A. Analytical technique.
B. Separation of the platinum metals from other elements.
C. Resolution of the platinum group into subgroups.
D. Separation of binary mixtures of the platinum metals.

For ease of reference, however, the whole of the rest of the text of §§ III to VIII will be subdivided into paragraphs provided with consecutive reference numbers (not letters) in arabic figures.

## A. ANALYTICAL TECHNIQUE.

(1) *Importance of Dry Assaying in the Determination of the Platinum Metals.*—The solubility of the platinum metals in molten lead offers the most convenient—and usually the only—means of quantitatively separating them from vastly preponderating amounts of base-metal compounds and siliceous material. Hence their determination in low-grade ores and by-products is inseparably connected with dry assaying, *i.e.* with the same smelting processes as are employed for the determination of gold and silver. The principal operations in this branch of assaying are crucible fusion, roasting, scorification, cupellation, and acid parting, and the laboratory must comprise a complete installation for the performance of these manipulations. To go into the details of dry assaying is beyond the scope of this manual, but it may be remarked that a skilful and experienced assayer is required to deal with the complex materials encountered in actual practice, and liable to contain all the members of the platinum group as well as gold and silver.

(2) *Treatment of the Lead Button.*—The lead button obtained by crucible fusion may contain copper, bismuth, antimony, selenium, tellurium, nickel, etc. in addition to the noble metals. If considered desirable, it may be purified by single or double scorification. The removal of any base metals found in the lead button may be effected by cupellation with excess of silver (4, ***below***) if practicable, or by the wet methods given ***below***.

The action of molten lead on the platinum metals is of great practical importance. The resultant lead button contains iridium, ruthenium, and osmium in an acid-insoluble form, while platinum, palladium, and rhodium can be obtained in solution by appropriate treatment, together with the lead and other base metals.

The lead button is dissolved in hot 15 per cent. nitric acid, the solution filtered, the washed residue returned to the beaker (*A*) together with the filter, and the latter destroyed by heating with 10 ml. of strong sulphuric acid and a few drops of nitric acid if necessary. While this operation is in progress, the filtrate is heated to about 80° C., stirred, and precipitated with sulphuric acid (1 : 3 water) in moderate excess. When cool, the liquid is filtered under slight suction and the washed lead sulphate rejected.[1]

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[1] The principle of fractional precipitation is also applied in the separation of Tannin Group A from Tannin Group B (**XIII**, § III, *d*).

The filtrate is evaporated to about 25 ml. and added to beaker *A*, which is then heated until the sulphuric acid fumes strongly. After cooling somewhat, 5 g. of solid ammonium sulphate is added, the beaker covered, and the acid liquor vigorously boiled for 10 to 15 minutes. When cold, the mass is taken up in 75 ml. of water, and the liquid boiled for a short time and set aside overnight. The solution is filtered and the residue washed with 0·5 per cent. sulphuric acid; the filtrate (beaker *B*) is reserved.

The residue consists of crystalline iridium, ruthenium, and osmium possibly alloyed with iron, spongy platinum, and lead sulphate showing a yellow to buff colour due to a little occluded rhodium. It is treated with a minimum of hot ammonium acetate solution to dissolve the lead sulphate, the filtered solution reprecipitated with a moderate excess of sulphuric acid, set aside overnight, and the lead sulphate (which is now white) filtered off; the filtrate is evaporated to very small bulk for the elimination of the acetic acid, diluted, and added to beaker *B*.

The residue freed from lead by ammonium acetate is returned to beaker *A* together with the filter, treated with 100 ml. of 15 per cent. *aqua regia*,[2] and the covered beaker kept on a hot-plate for an hour or more. The extract, containing platinum and gold, is filtered through a 9-cm. close-textured paper into a beaker (*C*) and the residue collected and washed with warm water, care being taken to ensure the complete transfer of the heavy microcrystalline residue of iridium, etc. to the filter. The beaker should be secured in an inclined position over the funnel, otherwise some of the minute glittering particles obstinately cling to the bottom of the beaker. While in this position the beaker should be flushed some 20 times with warm water, which need not be added to the filtrate. The filter-paper is transferred to a porcelain crucible and gently charred on an asbestos mat; the carbon is then burned off at the lowest possible temperature, so as to avoid loss of osmium. If the osmium content is at all substantial, it is always advisable first to carry out a peroxide fusion (18) and remove the osmium by distillation, rather than to start with the concentration of the noble metals into a lead button (41, γ).

The above operations yield three fractions: (*a*) a sulphate solution of palladium, rhodium, possibly silver, copper, bismuth, etc. (beaker *B*); (*b*) an *aqua-regia* solution of platinum and gold, and perhaps a little palladium and rhodium (beaker *C*—28, *below*); and (*c*) a residue of iridium, ruthenium, and osmium (iron) (18, *below*), sometimes contaminated with a little silver chloride.

The platinum metals contained in the acid sulphate solution (beaker *B*) are recovered either by a combination process involving cupellation (4, *below*), if the amount of rhodium and palladium present is not unduly high, or by a wet method (33).

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[1] The precipitate is free from platinum and palladium, and also from rhodium unless present in large amounts; in this case the lead nitrate solution is deep yellow to orange-yellow. If considered advisable, the lead sulphate may be tested for rhodium, etc. by crucible fusion with litharge, fluxes, and 1 to 2 g. of silver, cupellation of the lead button, solution of the silver bead in nitric acid, and fusion of the silver nitrate (6, *below*).

[2] 110 ml. of hydrochloric acid and 40 ml. of nitric acid diluted to 1000 ml.

*Combination process.* The hot sulphate solution is first treated with a small excess of hydrochloric acid if silver has to be determined; the silver chloride is left to settle, collected, and purified if contaminated with palladium (25, β). The solution free from silver is heated and precipitated exhaustively with pure powdered zinc until the precipitate has coagulated, when the action is allowed to proceed until all the zinc has dissolved. The precipitate is collected, washed with hot water, dried, detached from the filter, the paper ignited, and the ash added to the precipitate, which is wrapped in sheet lead, and cupelled with granulated lead and the necessary excess of silver (4, γ). If much copper is present, scorification should precede cupellation.

(3) *Fusion with Lead in a Carbon Crucible.*—The platinum metals may be concentrated into a lead button either by crucible fusion with litharge and reducing fluxes, the standard procedure for the assay of low-grade ores and impure by-products; or, if the mixed platinum metals have been isolated by a wet method, by fusion with lead in a small cylindrical crucible of purified gas-carbon. The metallic sponge is wrapped in pure sheet lead as used for gold and silver assaying.[1] The ratio of lead to noble metals should be 20 : 1. The carbon crucible, covered with a well-fitting lid, is placed inside a small fireclay pot, which is then filled with broken-up charcoal free from powder. The clay pot, covered with a lid of the same material, is heated in a closed muffle for an hour at a temperature not exceeding 1000° C. The resultant lead button is extracted with acids as described under (2), *above.*

(4) *Cupellation with Silver.*—Cupellation of the lead button (*cf.* 2, *above*) with excess of silver for the removal of lead, copper, bismuth, tellurium, etc. is a very advantageous procedure of restricted applicability.

(α) It is not admissible where osmium is involved, because this metal is partly or wholly volatilized as the tetroxide during the later stages of cupellation.

(β) In the case of ruthenium, rhodium, and iridium, it is limited to materials containing very small quantities of these three metals, because they oxidize more or less readily, the oxides staining the cupel and forming a brittle coating on the silver bead. A large excess of silver tends to counteract oxidation by keeping the metals in solution. Roughly speaking, the sum of the three noble metals should not exceed 0·02 g. in a silver bead weighing at least 3 g.

(γ) The concentration of platinum and palladium (with or without gold) into a silver bead by cupellation is very satisfactory. All that is required is a suitable excess of silver (at least 30 parts to 1 of platinum and palladium) to prevent solidification of the bead before all the lead has been oxidized.

(δ) When ores rich in sulphide minerals of nickel and copper are treated by crucible fusion, there results a lead button containing much nickel and copper, which cannot be completely removed by scorification. Such buttons upon cupellation yield a greenish-black scoria surrounding the silver bead, containing minute prills of silver and retaining rhodium and ruthenium, which would normally form a black incrustation on the bead. Nickel-copper ores should therefore be treated by a combination process (§ VII, 90, *a*).

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[1] This procedure applies also to the commercial platinum metals or their alloys in the form of wire, sheet, granules, etc.

(5) *Nitric-acid Parting of Silver Bead.*—A silver bead containing only iridium, rhodium, and ruthenium in small quantities (*cf.* 4, *β*, *above*) may be parted by boiling with dilute nitric acid (1 : 2 water), the partly oxidized platinum metals remaining as an insoluble residue, which is collected, washed with hot water, ignited, reduced (13), and weighed. If platinum and palladium are also present, Procedure (6) should be applied.

(6) *Fusion of Silver Nitrate.*—Palladium alloyed with silver is soluble in nitric acid. Platinum, although insoluble in nitric acid, dissolves to a brown to black colloidal solution when silver-rich platinum-silver alloys are boiled with nitric acid.

The most minute quantities of platinum and palladium are readily recoverable from large quantities of silver by a very simple procedure, *viz.* solution of the metal in nitric acid, evaporation, fusion of the silver nitrate [1] (m.p. 209° C.), and solution of the product in hot water, a process used on the large scale in the purification of silver nitrate, and applicable to the separation of silver from all the platinum metals. The latter remain insoluble, while silver nitrate goes into solution. A silver bead weighing at least 1 g. should be aimed at, and there should be a fiftyfold excess of silver over the other noble metals; a greater excess of silver is desirable, as this gives a fluid nitrate melt leading to a cleaner separation.

The silver bead obtained by cupellation is dissolved in nitric acid (1 : 1) in a small squat beaker of such size that the silver nitrate obtained by evaporation to dryness completely covers the bottom of the beaker. Any residue insoluble in nitric acid is disregarded at this stage, as it will be recovered after the fusion. When all the nitric acid has been expelled, the beaker is placed on an asbestos mat and gently heated with a rose burner until the salt is completely fused. If small crystals of unfused silver nitrate adhere to the sides of the beaker, they should be fused by gentle application of a small waving flame. After 1 to 2 minutes' fusion, the beaker is removed from the heat and set aside till quite cold; the silver nitrate is then dissolved in hot water, and the solution passed through a small filter. The residue is washed with hot water till free from dissolved silver and rinsed back into the beaker; the filter is cleaned with hot dilute *aqua regia*, and reserved. The residue is then digested with *aqua regia* (1 : 1 water), when it will dissolve completely if only platinum and palladium are present. The solution is evaporated to dryness on a water-bath, and the residue freed from nitric acid by double evaporation with hydrochloric acid. The last residue is taken up in warm water, and the solution filtered through the same filter fitted with a small pad of filter-pulp for the removal of a little silver chloride, which is washed with warm water. Platinum and palladium are separated as under (52).

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[1] W. Crookes, *Select Methods of Chemical Analysis*, 4th edition, 1905, pp. 273 and 323.

If, on the other hand, a dark residue is left after digestion with *aqua regia*, iridium, ruthenium, and rhodium may be present. The residue is collected (platinum and palladium passing into the filtrate), washed first with water, then with dilute ammonia (which is caught separately and rejected), ignited, and reduced. If rhodium preponderates, the residue should be fused with lead (3, *above*); if iridium or ruthenium preponderates, fusion with sodium peroxide (18) is applied.

(7) *Sulphuric-acid Parting of Silver Bead.*—This operation is restricted to platinum-silver alloys rich in silver. If it is intended to part platinum-rich alloys in this manner, they should be cupelled with more silver so as to yield a bead containing at least 10 parts of silver to 1 of platinum. The bead is flattened by hammering and boiled with slightly diluted sulphuric acid (9 : 1 water), the boiling being continued for a few minutes after the evolution of sulphur dioxide has ceased. The acid, while still warm, is cautiously diluted with a jet of cold water introduced through the spout of the covered beaker. The hot solution is filtered, and the residual platinum thoroughly washed with boiling water, transferred to a small beaker, and treated as under (6), *above*, by solution in *aqua regia*, double evaporation with hydrochloric acid, and filtration through a small filter-pad for the removal of any silver chloride, etc.

(8) *Fusion with Silver in an Annealing Cup.*[1]—This operation is quite different from cupellation with silver (4, *above*), and is carried out only for the purpose of determining the "sand," or non-metallic fraction, in native platinum and osmiridium.

Two g. of ore and 7 to 10 g. of pure silver (accurately weighed) are placed in an annealing cup previously glazed on the inside with borax, and covered with about 10 g. of borax glass. The cup is heated above the melting-point of silver in a muffle for half an hour, allowed to cool, broken, the silver button cleaned with hydrochloric and dilute hydrofluoric acids, and weighed. The increase over the weight of the silver represents the metallic portion of the ore, the "sand" being found by difference.

Native platinum, being an alloy of platinum, iron, and subordinate amounts of other metals (§ I, *a*, 1), is not affected by fusion with silver, and hence remains insoluble, along with osmiridium and finely divided gold, when the silver button is attacked with nitric acid.

(9) *Solution in Aqua Regia.*—Of the noble metals, only platinum, palladium, and gold are completely soluble in *aqua regia* (3 volumes of hydrochloric acid to 1 of nitric acid). Platinum is converted partly into chloroplatinic acid, $H_2PtCl_6$, and partly into nitrosyl chloroplatinate, $(NO)_2PtCl_6$. The latter compound, as well as the excess of nitric acid used, are undesirable in subsequent work, and must always be eliminated. This is done by evaporation of the solution on a water-bath until the syrupy residue barely smells of acid, addition of a small proportion of hot water followed by strong hydrochloric acid, and evaporation as before. The second residue is once more treated with water and hydrochloric acid, and again evaporated until all the acid is expelled. The residue from the last evaporation is normally free from nitrous compounds. Some operators add sodium chloride in

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[1] H. Ste. C. Deville and H. Debray, *Ann. Chim. Phys.* (3), 1859, **56**, 439.

slight excess over the quantity required to form sodium chloroplatinate, $Na_2PtCl_6$, prior to evaporation with hydrochloric acid. In either case, the last evaporation residue is taken up with 0·5N. hydrochloric acid.

Palladium dissolves in *aqua regia* with the formation of deep red chloropalladic acid, $H_2PdCl_6$. Upon evaporation with hydrochloric acid (as for platinum, *above*), the compound loses chlorine, becoming converted into brown chloropalladous acid, $H_2PdCl_4$. No nitrosyl compound is formed. Chloropalladous acid has a tendency to hydrolyse in aqueous solution, with precipitation of basic compounds; it should be taken up with dilute hydrochloric acid.

Iridium and rhodium, though more or less insoluble in *aqua regia* (depending upon the degree of subdivision—the compact metals are not attacked), are soluble if alloyed with a large excess of platinum. The solution of iridiferous platinum in *aqua regia* is light to deep brown.

The older analytical methods for the separation of platinum from some of its congeners were based on the principle of selective solution, the mixed ignited metals obtained by precipitation being digested with dilute *aqua regia* until a fresh portion of acid remained colourless. The results thus obtained are not sufficiently reliable for accurate work, and it is highly desirable to discard such methods altogether. An exception may be made for ignited precipitates weighing only a few mg. and consisting chiefly of iridium with a little palladium and platinum (such as $P^{1a}$, 11, *below*). Upon digestion with dilute *aqua regia* (1 : 3 water), they leave a residue of substantially pure iridium.

(10) *Precipitation with Ammonium Chloride.*—Ammonium chloride is a specific reagent for the hexachloro-acids of platinum, iridium, and palladium, with which it forms yellow, black, and scarlet crystalline precipitates respectively (§ II, *c*, 4, 5, and 6). The salt is employed as a quantitative reagent for these metals; certain objections against its use as such have been answered in the preamble to § III.

Ammonium chloride is most usually employed as a precipitant for platinum and iridium, either alone or in admixture, palladium if present having been converted into chloropalladous acid. In order to minimize coprecipitation of other metals, it is advisable first to add a dilute solution of the reagent drop by drop in slight excess to the warm solution from (9)—or (21)—during continuous agitation, the bulk of the platinum and iridium being precipitated. The liquid is left to cool, and diluted with an equal volume of saturated ammonium chloride solution; if this leads to an unduly large volume of solution, a suitable quantity of solid A.R. ammonium chloride may be added instead. The salt used for this purpose should be recrystallized by the operator, for the removal of any insoluble particles. The solution is set aside in a cool place for some hours or overnight, and filtered. The precipitate, $P^1$, is collected, washed with half-saturated ammonium chloride solution, and reserved.

The filtrate is concentrated in the original beaker on a water-bath or hot-plate, with the occasional addition of a drop of sodium chlorate solution (to oxidize any chloriridite), until ammonium chloride begins to crystallize out at the surface. While still hot, the liquid is stirred and cautiously treated with a little cold water to redissolve the crystals, and set aside overnight to cool.

The clear solution is decanted through a smaller filter, and the small dark precipitate, $P^{1a}$ (mostly chloriridate), collected and washed as before.

The precipitation of platinum and iridium by the above process is quantitative within the limits of experimental error. If obtained from more or less pure solutions, the precipitates are sufficiently pure to be converted to metal by ignition (12, *below*). If, however, small quantities of palladium and rhodium and substantial quantities of base metals (*e.g.* iron, copper, nickel, bismuth) are present, it is advisable to purify the precipitate $P^1$ by the chlorine process (11, *below*).

(11) *The Chlorine Process.*[1]—Small quantities of ammonium chloroplatinate (chloriridate) may be purified by simple recrystallization, the precipitate being washed on the filter with boiling water until completely dissolved, and the washings evaporated to small bulk, with subsequent addition of a little ammonium chloride after cooling. In the case of fairly large precipitates, their sparing solubility renders the above procedure impracticable on account of the large volume of water required. The simplest way to overcome the difficulty is to reconvert the precipitate into hexachloro-acids by the action of a current of chlorine upon its suspension in boiling water.

The washed precipitate produced by ammonium chloride (*e.g.* $P^1$, 10, *above*) is rinsed back into the original beaker (400 ml.), and the filter completely cleaned with boiling water. The liquid (about 150 ml. for 1 g. of platinum metals), slightly acidified with hydrochloric acid, is vigorously boiled, and kept stirred by means of a glass tube through which a brisk current of chlorine is introduced (the gas should not be passed through the cold solution, as there would be a risk of explosion due to the formation of nitrogen chloride). The precipitate dissolves readily, usually in a few minutes. When solution has taken place the chlorine current is interrupted, the tube washed down with hot water, and the solution placed on a hot-plate for evaporation after addition of just enough ammonium chloride to combine with the platinum (iridium) (6 ml. of 10 per cent. solution for 1 g. of metal). When the bulk has been reduced to about 20 ml., the solution is left to cool and diluted with an equal bulk of half-saturated ammonium chloride solution. After standing for a few hours the coarsely crystalline precipitate, $P^2$, is collected, washed with the same ammonium chloride solution, and transferred to a tared Rose crucible. It contains the great bulk of the platinum and iridium free from other metals.

In the practical application of the chlorine process, the filtrate from $P^2$, containing the metals occluded in $P^1$, is added to the filtrate from $P^1$, and worked up for the minor platinum-iridium fraction $P^{1a}$ as under (10), as well as for palladium and rhodium—see (49).

(12) *Ignition of Precipitates Produced by Ammonium Chloride.*—The ignition of the " double chlorides " of the platinum metals has to be effected with great care so that loss by decrepitation may be avoided. In all cases, the washed precipitate is carefully wrapped in the wet filter, the edges of the

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[1] W. R. Schoeller, *Analyst*, 1930, **55**, 551.

paper being folded over the single layer and the folds pressed against the bottom of the crucible, with the threefold layer of paper uppermost. The crucible is heated on an asbestos mat over a small flame until the paper is dry. The heat is then raised very slightly to cause a barely visible evolution of ammonium-chloride fumes. With large precipitates the procedure takes several hours, but requires very little supervision. When the ammonium salt has been expelled, the charred paper is burned away at a low temperature, after which the heat is raised to redness. The ignited precipitate is next reduced to metal (13).

(13) *Reduction of Ignited Precipitates.*—Osmium precipitates (§ IV, 58) cannot be ignited in air without volatilization of osmium tetroxide. Platinum precipitates free from other fixed constituents, when ignited in air, leave metallic platinum, while sulphide, hydroxide, and ammonium-chloride precipitates of the remaining four metals are left either wholly or partly as oxides, which must be reduced to the metallic state before being weighed.

Reduction is carried out by means of hydrogen in a tared Rose crucible; the precipitate, after having been ignited in air, is left to cool somewhat, the crucible is covered, and a slow current of hydrogen is admitted through a tube connected by a three-way stopcock to a supply of hydrogen and carbon dioxide. The crucible is heated to dull redness, kept at this temperature for a few minutes, and allowed to cool to 200° to 300° C., when the hydrogen in the crucible is displaced by a slow current of carbon dioxide, in which the metal is allowed to cool to room temperature. In technical work, the reduction to metal may be effected by coal-gas, the small luminous flame of a Bunsen burner being directed upon the hot precipitate while the crucible is in a slanting position, so that the escaping gas burns at the mouth of the crucible. Reduction takes place with incandescence, and the dark or black oxide is converted into grey metal. This must be allowed to cool in the gas as a protection from oxidation.

(14) *Hydrogen-sulphide precipitation* is strongly advocated by the investigators of the U.S. Bureau of Standards, but we find ourselves unable to recommend the procedure unreservedly. In the time-honoured grouping dear to the teaching profession, the platinum metals are assigned to the "second" or hydrogen-sulphide group; but to describe them as unruly members of that class of elements conveys a better idea of their behaviour towards the group reagent. The difficulties encountered in the quantitative precipitation of the platinum metals by hydrogen sulphide are due to the pronounced tendency of these elements to form comparatively stable complexes. Palladous sulphide (PdS) is most readily precipitated, platinic sulphide less so, while the precipitation of rhodium and especially of iridium by hydrogen sulphide is more erratic. The behaviour of ruthenium towards hydrogen sulphide recalls that of molybdenum, partial reduction being liable to occur, as revealed by the blue colour of the solution. We successfully apply a modified sulphide process for the gravimetric determination of ruthenium and osmium, but not for their separation from other metals (§ IV, 59 and 60).

With rhodium and iridium, we have at times achieved quantitative precipitation, whilst at others even pressure precipitation failed to bring about the desired result. E. Wichers[1] states that "the complete precipitation of iridium requires two to three hours' treatment with a fairly rapid stream of hydrogen sulphide in a solution kept just below the boiling-point," an acidity of 20 per cent. by volume of hydrochloric acid being prescribed. Even if this malodorous practice is usually successful, the operator has no other more certain means of ascertaining the completeness of the precipitation than further prolonged treatment of the filtrate with the gas. For the present we still consider hydrogen sulphide a reagent of doubtful efficacy for the recovery of these valuable metals under the arduous conditions of actual practice.

(15) *Zinc precipitation* is a convenient means of recovering rhodium, palladium, platinum, and ruthenium from solutions, and of separating them from base metals, etc. not precipitated by zinc. The recovery of iridium by displacement with zinc is rarely complete. The acid chloride solution free from iridium and nitrates is heated to about 80° C. and treated with excess of chemically pure, powdered zinc. When the ferric salt has been reduced, the action is allowed to proceed for some time until it becomes sluggish owing to neutralization of the acid, the zinc being in excess. Strong hydrochloric acid is then added in portions to the hot solution until the zinc is dissolved. The precipitate is collected on a loose filter and washed twice without delay with N. hydrochloric acid, the washing being completed with 0·1N. acid.

(16) *The nitrite process* is a valuable method for separating large or small amounts of rhodium, iridium, platinum, and ruthenium from small quantities of base metals (lead, bismuth, copper, iron, nickel, etc.). If the base metals are present in quantity, the bulky precipitate of hydroxides (basic carbonates) adsorbs a large proportion of the noble metals. Double treatment must be applied in any case. The process does not answer so well for palladium, because the double nitrite of that metal is less stable in the boiling alkaline solution; hence palladium may be found in the precipitate after double treatment. The precipitate may be tested for palladium by solution in dilute hydrochloric acid and precipitation with dimethylglyoxime (§ IV, 68), with or without intervening precipitation on zinc (33).

The chloride solution should be free from ammonium chloride. If this salt is present, it must be destroyed by boiling in a large flask with a copious excess of strong nitric acid (30 to 50 ml.):

$$2NH_4Cl + 6HNO_3 = 2HCl + 6NO_2 + N_2 + 6H_2O.$$

When the volume has been reduced to about 25 ml., the solution is transferred to a beaker, evaporated to dryness, and the residue evaporated twice with a little hydrochloric acid. The final residue is dissolved in hot water.

The hot, nearly neutral solution (100 ml.) is treated with 5 g. of sodium nitrite and set aside on a covered water-bath for an hour. It is then cautiously treated with sodium hydroxide drop by drop until the precipitate no longer increases in bulk, and flocculates readily. This is collected, washed with hot water, dissolved in hydrochloric acid, and the precipitation from the neutralized solution is repeated. The combined nitrite filtrate is acidified with hydrochloric acid and evaporated to dryness before being subjected to further manipulation.

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[1] Hillebrand and Lundell, *op. cit.*, p. 276.

In the absence of platinum, a preliminary separation of rhodium and iridium from much copper may be effected by bromate hydrolysis (47). The precipitate, containing the platinum metals, bismuth, and a little copper, is dissolved in hydrochloric acid; the solution is neutralized with sodium hydroxide, and submitted to the nitrite treatment.

(17) *Precipitation with Titanous Salt.*—Solutions of platinum, palladium, and rhodium are reduced by titanous salt with precipitation of the metal, while iridium solutions are not precipitated, reduction proceeding only to the iridous state. Copper in large amounts interferes, being also precipitated; if small, it is held in solution at high acidity. Bismuth is also precipitated. The procedure is more expeditious than zinc precipitation, but the precipitate may be contaminated with titania unless the acid concentration is very high. Precipitation may be effected with titanous chloride, but we favour titanous sulphate, which is prepared by electrolytic reduction at a mercury cathode of titanic sulphate solution (obtained from a bisulphate melt of titanic oxide, or from potassium titanium oxalate by evaporation with sulphuric acid until strong white fumes are evolved).

The solution under treatment is acidified with 30 to 40 per cent. by volume of sulphuric acid, boiled, and treated with a decided excess of the titanous salt solution. When the precipitate has coagulated, the liquid is diluted with an equal volume of water, and filtered. The precipitate is washed with 5 per cent. sulphuric acid, the beaker and rod being cleaned by rubbing with filter-pulp. Filter and precipitate are returned to the beaker; for the further treatment thereof see (50).

(18) *Fusion with Sodium Peroxide.*[1]—This is the third and last important procedure for attacking materials containing metals of the platinum group, the other two being solution in *aqua regia* (9) and fusion with lead, or litharge and fluxes (2 and 3).

Fusion with sodium peroxide forms the first step in the separation and determination of osmium, ruthenium, and iridium. Materials rich in rhodium must be attacked by fusion with lead or litharge, while those in which platinum and palladium preponderate may be decomposed by *aqua regia.*

The sodium-peroxide fusion is carried out in a nickel crucible; the material to be fused must be in the state of very fine powder. Native osmiridium, which defies all attempts at crushing, is converted into fine powder after fusion with zinc (§ VIII, 93). The powder is thoroughly mixed with 15 to 20 g. of sodium peroxide; 2 or 3 g. of powdered sodium hydroxide may be added. The crucible is gradually heated on an asbestos mat until the mixture sinters. It is kept in this condition for 1 to 3 hours, according to the amount of noble metals present, after which it is heated more strongly, passing from a pasty to a viscous mass, which is finally converted into a fluid melt by stronger heating on a triangle. The crucible is now rotated at frequent intervals, and finally heated for a short time at a bright red heat. The second fusion period occupies about the same time as the first (sintering).

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[1] E. Leidié and M. Quennessen, *Bull. Soc. chim.*, 1902, **27**, 181.

The cold melt is disintegrated with cold water in a 600-ml. beaker, the crucible removed with the aid of tongs, cleaned with a rubber-tipped glass rod, and discarded. By weighing it before and after fusion, the operator can ascertain the amount of nickel introduced into the assay. Some prefer coating the inside of the nickel crucible with a layer of fused sodium carbonate for the purpose of decreasing the attack on the metal. Distillation in one form or another being the next step, the alkaline suspension is quantitatively transferred to a distillation flask (20, *below*).

(19) *Fusion with Potassium Hydroxide and Nitrate.*—This is the older fusion procedure of Deville and Stas,[1] now displaced by fusion with sodium peroxide (18). It is useful in a few cases, such as the determination of small amounts of iron in iridium or ruthenium, since the iron blank in a peroxide fusion, derived from the nickel crucible, may amount to several mg.

Deville and Stas's process is carried out in a crucible of pure gold. The fine powder is added to the previously melted and solidified flux (3 parts of potassium nitrate and 12 of hydroxide). The crucible, covered with a gold lid, is heated for 3 hours at 950° C. The mass is taken up in water, and the alkaline suspension treated as under (18).

(20) *Distillation Apparatus for Osmium and Ruthenium.*—These two elements can be separated from the other four platinum metals, from all other elements in general, and from one another, by distillation, a fact which greatly simplifies the analysis of the platinum group.

The distillation and absorption flasks used in these operations must be glass-stoppered, and should be connected by ground-glass joints. For practical purposes, however, it is sufficient to use ordinary glass-stoppered wash-bottles, the short or blowing-in tubes of which are made to bend downwards at an angle of 30°, while the longer tubes (the drawn-out jets of which are cut off) are given an upward bend of 30°. In this manner the blowing-in tube becomes the exit tube, and the tube which carries the jet, the inlet tube. The ends of the glass tubes should be cut straight and carefully rounded off in a small flame, so as to give glass-to-glass joints sealed with a film of water when the flasks are connected with stout wetted rubber tubing. Flasks of 1000, 500, and 250 ml. capacity are required.

The complete train is composed of three parts, *viz.* the distillation train, the ruthenium absorption train, and the osmium absorption train.

*Distillation train.* This consists of a gas-washing bottle containing water, for judging and regulating the speed of the gas current circulating through the train. This bottle is connected to the inlet tube of the distillation flask, of 1000 ml. capacity for high-grade material (*e.g.* osmiridium); a smaller flask is used for poorer ores, residues, etc.

*Ruthenium train.* The train consists of a series of four absorption flasks, the first of which is connected to the distillation flask. They are charged with dilute hydrochloric acid as follows:

No. 1 (capacity 500 ml.) : 50 ml. HCl (1 : 1);
No. 2 (capacity 500 ml.) : 50 ml. HCl (1 : 2 water);
No. 3 (capacity 500 ml.) : 50 ml. HCl (1 : 2 water);
No. 4 (capacity 250 ml.) : 20 ml. HCl (1 : 4 water).

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[1] H. Ste. C. Deville and J. S. Stas, *De l'Analyse du Platine iridié*, Paris, 1878.

Receivers of 250 ml. capacity may be used for small quantities, the amount of acid being suitably reduced.

*Osmium train.* This is composed of two absorption flasks, *viz.* No. 5 (capacity 1000 ml.), immersed in cold water; it contains a solution of 25 g. of sodium hydroxide and 25 ml. of alcohol in 500 ml. of water; and No. 6 (capacity 250 ml.), containing 50 ml. of the same solution as No. 5.

*Heat supply: suction.* The distillation flask, as well as the ruthenium receivers Nos. 1 to 3, are placed on stands over Bunsen burners. The whole train must be very carefully adjusted so that all tubes meet glass to glass. The exit tube of the last flask (either No. 4 or No. 6) is connected to a suction pump when a current of air is required.

The apparatus can be used for three distinct operations:

(*a*) Ruthenium distillations: the distillation train is connected to the ruthenium train.

(*b*) Osmium distillations: the distillation train is connected to the osmium train. A short cooler may be inserted between the distillation flask and receiver No. 5.

(*c*) Ruthenium-osmium distillations: the distillation train is connected to the ruthenium and osmium trains in the order given *above*. The distillations will be described under C, (42) to (44).

(21) *Recovery of the Non-volatile Platinum Metals from the Residual Solution.*—Whichever distillation method has been employed, the procedure for recovering the metals other than osmium and ruthenium from the residual solution is as follows (in the case of chlorine distillations, the second or minor ruthenium fraction may be included in this procedure):

The hot liquid left in the distillation flask is treated with a solution of 10 g. of sodium hydroxide and 20 ml. of alcohol, boiled for 5 minutes, and transferred to a 600- or 800-ml. beaker; the distillation flask is thoroughly rinsed with hot water, and discarded. The metals of the platinum group are thus precipitated as hydroxides, together with the nickel resulting from the attack of the sodium peroxide on the crucible. The liquid is left to settle, and decanted through a 15-cm. filter. Beaker and precipitate are washed several times with hot water, which removes the bulk of the sodium salts. The precipitate is returned to the beaker with hot water; finally the filter is thoroughly washed with hot hydrochloric acid (1 : 1), and discarded. The suspension is evaporated to dryness with 15 ml. of hydrochloric and 5 ml. of nitric acid on a water-bath. The dry residue is taken up with hot dilute hydrochloric acid, and the solution filtered through a 9-cm. paper into a squat 250-ml. beaker; the residue (silica resulting from the action of the alkali on the glass, generally coloured by a little adsorbed iridium hydroxide) is collected, washed with hot water, ignited strongly, and treated with hydrofluoric and hydrochloric acids in a small gold or platinum dish; it is then collected on a small filter, washed, and transferred to a tared porcelain crucible (*A*). The filtrate is worked up as directed under C, (43, $\beta$).

(22) *Fusion with Sodium Chloride in a Current of Chlorine.*[1]—This is a procedure of general applicability to the platinum metals, which is most useful in the examination for purity of ignited rhodium precipitates. It

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[1] F. Wöhler, *Pogg. Ann.*, 1834, 31, 161.

introduces no impurities, but is tedious for any but small quantities of material.

The finely divided metal is intimately mixed with two parts of sodium chloride by trituration in a small agate mortar. The mixture is quantitatively transferred to a Rose crucible and heated in a current of undried chlorine, gently at first, then more strongly, and finally with the full flame of the Bunsen burner above the melting-point of the salt (800° C.). After cooling, the melt is dissolved in water, in which it should dissolve without leaving any dark insoluble residue. Should this be the case, then the insoluble matter must be filtered off, washed, ignited, reduced (13), again triturated with sodium chloride, and the fusion process repeated.

## B. Separation of the Platinum Metals from Other Elements.

(23) *From Silver.*—Of the six platinum metals, only rhodium and palladium form normal nitrates, and may therefore co-exist in solution with silver nitrate. The separation of these two metals from silver will therefore have to be considered (24 and 25, *below*). The remaining separation cases are those presented by a silver bead obtained by cupellation, liable to contain five platinum metals (osmium is excluded: 4, *α*) and gold. Such beads may be treated with either nitric (5 and 6) or sulphuric (7) acid. The determination of silver in the presence of the platinum metals will be described under (26), *below.*

(24) *Rhodium from Silver.*—The boiling nitrate (or sulphate) solution is precipitated, drop by drop, with very dilute hydrochloric acid until no further precipitate forms. The silver chloride is allowed to settle, filtered off, and washed as usual. The filtrate is evaporated with sulphuric acid for the removal of nitric acid (sulphate solutions free from nitric acid need not be treated in this manner), and the rhodium is precipitated with hydrazine or magnesium (§ IV, 71, 73).

(25) *Palladium from Silver: Authors' Method.*[1]—When a nitrate or sulphate solution of palladium and silver is treated with hydrochloric acid, the silver chloride carries down palladium, and is thereby coloured pink to brown. We have shown that silver chloride free from palladium can be obtained in one precipitation if the palladium is converted into a tetramminepalladous salt prior to the precipitation of silver chloride.

(*α*) The hot solution of the nitrates is treated with ammonia until the precipitate first formed redissolves and the solution becomes colourless. A small piece of litmus-paper is dropped into the solution, which is slightly acidified with acetic acid, and treated while hot with dilute hydrochloric acid drop by drop, with constant stirring, until no further precipitate forms, after which it is left in the dark till clear. The precipitate is filtered by decantation and washed with very dilute nitric acid. The filtrate is treated with a little more acid and precipitated with dimethylglyoxime (46, *α*).

(*β*) In the case of a coloured precipitate of silver chloride containing palladium, the procedure is as follows: The precipitate is dissolved in a minimum excess of ammonia, and the hot solution slightly acidified with acetic acid. The silver is then precipitated as chloride as under (α).

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[1] Originally published in the first edition of this work.

(26) *Determination of Silver in the Presence of the Platinum Metals and Gold.*—The determination of silver in high-grade by-products, etc. cannot be carried out by the ordinary assay method, because a portion of the silver may remain insoluble in the parting acid, while on the other hand part of the palladium and platinum are dissolved by the acid together with the bulk of the silver.

The lead button obtained by crucible fusion or scorification is cleaned and dissolved in hot 10 per cent. nitric acid; the residue is collected and washed with hot water. The filtrate is precipitated with a slight excess of hydrochloric acid, the precipitated silver chloride being collected after standing overnight. If pink or brown, it is dissolved in ammonia and reprecipitated (25, β, *above*).

The residue insoluble in nitric acid (if the material is very high in silver and rhodium) should be rescorified, and the second lead button treated as the first, yielding a second, small silver-chloride fraction.

The insoluble residue from the (first or second) lead button is returned to the beaker, and the filter destroyed by digestion with 10 to 15 ml. of strong sulphuric and small additions of nitric acid. When the organic matter has been eliminated, the covered beaker is strongly heated, the sulphuric acid being kept boiling for 15 minutes. After cooling, the warm acid is diluted with cold water, the lead sulphate left to settle, and the solution filtered; the filtrate is treated with a moderate excess of hydrochloric acid, when it usually yields a further crop of silver chloride (always so if the assay contains appreciable amounts of rhodium, in which case the sulphuric acid will acquire a yellow to brown colour).

The combined silver-chloride precipitates are gently ignited and cupelled with lead, giving a bead of pure silver, which is weighed.

(27) *From Gold: by Parting.*—The separation of gold from the platinum metals may be effected by a parting process with dilute *aqua regia*, *below*, or by precipitation of the gold by a reducing agent from a common chloride solution (28, 29, and 30).

When a silver bead containing other precious metals and excess of silver is parted with nitric acid, the silver dissolves, together with platinum and palladium, leaving a residue of finely divided gold, iridium, rhodium, and ruthenium. Treatment of the residue with dilute *aqua regia* (1 : 4 water) yields a solution of gold and a residue containing any of the other metals present. They may be collected, washed, ignited, and reduced (13).

(28) *From Gold: Ferrous-chloride Reduction.*—A variety of reagents is available for the reduction of auric chloride, *e.g.* sulphur dioxide, oxalic acid, ferrous salts, and the hydrochlorides of hydrazine and hydroxylamine. We give preference to ferrous chloride or, if the introduction of iron into the solution is undesirable, to the hydrazine salt.

The hot chloride solution, freed from nitric acid by double evaporation with hydrochloric acid, and containing one-fifth of its volume of hydrochloric acid, is treated drop by drop with a slight excess of a strong, freshly prepared solution of ferrous chloride free from ferric salt. The solution is set aside at room temperature until the precipitated gold has settled and the liquid above the precipitate has cleared. The precipitate is collected on a small close-textured filter and thoroughly washed with 2 per cent. hydrochloric acid. The separation of gold from iridium, rhodium, and ruthenium is quantitative in one operation. If platinum and palladium are present, the precipitate should be ignited, dissolved in *aqua regia*, the solution freed from nitric acid by evaporation and re-evaporation with hydrochloric acid, and the precipitation with ferrous chloride repeated.

(29) *From Gold: Hydrazine Reduction.*—The chloride solution freed from nitric acid (*cf.* 28) is diluted with an equal volume of strong hydrochloric acid, heated to boiling, and treated drop by drop with a freshly prepared 2 per cent. solution of hydrazine hydrochloride in slight excess. Otherwise the directions are the same as under (28), including retreatment of the precipitate in separations of gold from platinum and palladium. The filtrate from the gold is freed from precipitant either by evaporation to dryness, digestion of the residue with strong nitric acid, and renewed evaporation to dryness, followed by double evaporation with hydrochloric acid to destroy nitrates; or by boiling with sodium chlorate.

(30) *From Gold: Nitrite Reduction.*—In the separation of platinum metals from base metals by means of sodium nitrite (16), gold if present in the solution is reduced and precipitated together with the hydroxides and basic carbonates of the base metals.

(31) *From Gold: Ether Extraction.*—When an acid chloride solution containing gold and platinum metals is shaken with ether in a separator, the gold alone passes into the ethereal layer. The procedure is not recommended for strictly quantitative purposes, but is of qualitative interest.

(32) *Determination of Gold in the Presence of the Platinum Metals.*—For the determination of gold in ores, by-products, etc. containing members of the platinum group, the customary dry assay method must be modified. It is usually best to carry out one or more fusions in clay crucibles with litharge, fluxes, flour, and excess of silver, added as such or in the form of pure silver nitrate. The lead button is scorified if necessary, and cupelled. The resultant silver bead is dissolved in nitric acid (1 : 2 water); at the operator's discretion, the silver nitrate solution may be either decanted off and the residue well washed with warm water, or evaporated to dryness, the residual silver nitrate fused, dissolved in hot water, and the solution filtered (6). In the latter case, platinum and palladium remain with the gold, etc., and may be subsequently determined. The residue from either treatment is extracted with 15 per cent. *aqua regia*, which dissolves the whole of the gold; the solution is filtered if necessary, and treated as under (28) or (29), *above*.

(33) *From Silver, Gold, Lead, Copper, Bismuth, etc. after Fusion with Lead.*—The separation processes about to be described form the sequel of the operations aiming at the recovery of the platinum metals from the lead button obtained by crucible fusion or scorification. So far, the manipulations have yielded three fractions (*cf.* 2): (*a*) a sulphate solution of palladium and rhodium, with silver and base metals (beaker *B*); (*b*) an *aqua-regia* solution of platinum and gold (beaker *C*); and (*c*) the insoluble alloy of

iridium, ruthenium, and osmium. The treatment of the last has been discussed under (18); the three platinum metals contained in the two solutions *B* and *C* are separated from silver, gold, and all base metals as follows:

*Beaker C.* The *aqua-regia* solution is freed from nitric acid by evaporation followed by double evaporation with hydrochloric acid; the gold is precipitated with a slight excess of ferrous chloride (28, *above*). The filtrate is heated with a slight excess of sodium chlorate for the oxidation of iron and platinum, and precipitated with ammonium chloride (10). The chloroplatinate precipitate (*D*) is collected and, unless quite small, purified by the chlorine process (11). The filtrates from the chloroplatinate precipitates are combined and reserved (filtrate *E*).

*Beaker B.* The hot sulphate solution is treated with a small excess of dilute hydrochloric acid, and the silver chloride precipitate is left to settle, collected, and purified if contaminated with palladium (25, *β*). The filtrate or combined filtrate from the silver chloride is added to filtrate *E*, and treated exhaustively with pure zinc (15). The resultant precipitate contains all the palladium, rhodium, very little platinum, and copper, bismuth, tellurium, antimony, etc. It is filtered off, rinsed into a smaller beaker with hot water, the filter washed down with dilute *aqua regia* and ignited, and the ash added to the suspension. The precipitate is digested with *aqua regia* (1 : 1 water) on a water-bath until no further attack takes place; the black residue (*F*), if any, consisting of part of the rhodium in a state of purity,[1] is reserved.

The *aqua-regia* filtrate is evaporated to dryness, and the residue once more evaporated with hydrochloric acid. The last residue is taken up with a few drops of hydrochloric acid and 100 ml. of hot water, and submitted to the nitrite process (16) (double treatment). The combined filtrates (*G*) contain the balance of the rhodium, nearly the whole of the palladium, and traces of platinum; they are boiled down with excess of hydrochloric acid, and the solution evaporated to dryness.

It remains to ascertain the completeness of the separation by testing the precipitate of base-metal hydroxides obtained in the nitrite process. The precipitate is returned to the beaker, dissolved in hydrochloric acid, and the solution precipitated with zinc (15). The metallic precipitate thus obtained is treated by the combination process described under (2), which results in a silver bead containing the minute quantity of platinum metals (chiefly palladium) which had so far escaped recovery. The bead is dissolved in nitric acid, the resultant silver nitrate fused (6), dissolved in hot water, and the small dark residue collected and dissolved in dilute *aqua regia*. Should this attack prove incomplete, the residue therefrom is brought into solution by fusion with sodium chloride in chlorine (22). The small fraction recovered from the silver bead is added to filtrates *G*.

The products from the above operations are (in addition to the insoluble iridium-ruthenium-osmium alloy, silver chloride, and gold): *D*, a pure chloroplatinate precipitate representing the major platinum fraction; *F*, a pure rhodium fraction; and *G*, the mixed chlorides of palladium, rhodium, and a little platinum, free from other metals. The resolution of that ternary mixture will be described under C, (50).

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[1] The attack of an *unignited* metallic precipitate is not open to the objections raised under (9). In the present case, although the rhodium is partly soluble, the insoluble fraction retains no palladium or platinum; hence the accuracy of the subsequent separation of the dissolved metals is not vitiated by part of the rhodium remaining insoluble.

*Note.*—In the above scheme, the palladium could be precipitated with dimethylglyoxime from the *aqua-regia* solution prior to the application of the nitrite process. However, this would complicate the scheme by necessitating another evaporation of the filtrate with *aqua regia* for the purpose of destroying the excess of precipitant.

(34) *Rhodium and Palladium from Lead.*—As in the case of silver (23), the nitrates of rhodium and palladium may co-exist in solution with lead nitrate. The separation is effected by precipitation of lead as sulphate from a solution containing a minimum of free nitric acid, and freed therefrom if necessary by evaporation. The warm dilute solution is stirred, precipitated with 20 per cent. sulphuric acid in slight excess, and set aside overnight. The precipitate is dealt with in known manner.

The separation of palladium from lead is more satisfactory than that of rhodium, which induces less complete precipitation of the lead. The main lead-sulphate precipitate is free from rhodium unless this is present in quantity (*cf.* (2), footnote 1). The filtrate should be evaporated until fumes of sulphuric acid are evolved. After dilution, the small precipitate of lead sulphate (which is yellowish in colour) is filtered off, washed, and boiled with sodium carbonate solution; the carbonate precipitate is collected, dissolved in a little nitric acid, and the solution again precipitated with sulphuric acid. After standing overnight, the lead sulphate is filtered off, and the filtrate, containing the minor rhodium fraction, added to the bulk. Rhodium and palladium are recovered by precipitation with hydrazine (§ IV, 71), and separated by treatment with dilute *aqua regia*, etc. (50), the soluble rhodium fraction being once more precipitated with hydrazine after destruction of the excess of dimethylglyoxime.

(35) *Rhodium, Palladium, Iridium, and Platinum from Lead.*—The preceding paragraph (34) dealt with the precipitation of lead from nitrate solutions. Chloride solutions may contain the above four platinum metals, together with lead at a concentration limited by the sparing solubility of lead chloride. This may be removed by the addition of alcohol, but the separation of the lead is never complete; again, lead-chloride crystals depositing from a solution containing very small amounts of rhodium show a fine, delicate, pink to rose-red colour, which reveals the presence of rhodium in association with a large excess both of gold and of platinum (§ VI, 82, $\gamma$). The pink crystals must be regarded as a solid solution of rhodium chloride in lead chloride.

For the separation of lead from the platinum metals in chloride solution, recourse must be had to the nitrite method. If any lead chloride has separated, it is dissolved by heating, and dilution if necessary. The solution is approximately neutralized with sodium hydroxide, and treated as under (16). It is advantageous to have a little iron, bismuth or other base metal present to act as a collector for the lead.

(36) *From Copper: Thiocyanate Process.*[1]—In chloride solution, copper may be separated from platinum, palladium, iridium, and rhodium by double precipitation with ammonium thiocyanate and sulphurous acid. The procedure is restricted to quantities of copper not exceeding 0·1 g., but the solution may contain several grams of platinum metals in 200 ml. total bulk. The solution is treated with 20-ml. portions of saturated sulphur dioxide solution until it is pale yellow and smells strongly of the gas after digestion for half an hour on a water-bath; the solution is then neutralized with sodium hydroxide until a precipitate begins to form, treated with 6 to 10 drops of strong hydrochloric acid, and the copper precipitated with a 2 per cent. solution of ammonium thiocyanate in saturated sulphur dioxide solution (10 ml. per 0·05 g. of copper) added during continuous agitation. The cold solution is set aside overnight, and filtered through close-textured paper, which is washed with cold water containing a little sodium chloride. The filter is returned to the beaker, the precipitate dissolved in a small excess of nitric acid (1 : 3 water) by digestion on a steam-bath, the paper pulp filtered off, and the filtrate reprecipitated as described.

The platinum metals are in the combined filtrates from the copper precipitate, but a small fraction may remain in the paper pulp left after filtration of the first copper precipitate. The pulp is digested with *aqua regia*, and filtered off after addition of water, the filtrate being added to the bulk. The combined solutions are evaporated with *aqua regia*, and the residue evaporated twice with hydrochloric acid. Further treatment: see (47), *below*.

(37) *From Copper: Other Processes.*—The thiocyanate process (36) is not recommended for quantities of copper exceeding 0·1 g. Our own experience leads us to give preference to other separation methods. Platinum and iridium may be separated as " double chlorides " (10); palladium in substantial quantities as ammonium chloropalladate (§ IV, 69), or, if in small amounts, by dimethylglyoxime (46, *a*); rhodium by the nitrite method (16). The last may be used for separating all the platinum metals from copper as well as from lead (35) and bismuth (38).

(38) *From Bismuth.*—The essential data for the separation of bismuth from the platinum metals will be found under the following heads: (4) cupellation with silver; (10) precipitation with ammonium chloride (for platinum and iridium); (16) the nitrite process; and (46, *a*) precipitation of palladium by dimethylglyoxime.

Bismuth may also be precipitated as oxychloride by the usual process, but the precipitate has a tendency to occlude platinum metals. If not perfectly white, it should be dissolved in hydrochloric acid, and the precipitation repeated.

(39) *From Arsenic, Antimony, Tellurium, and Selenium.*—This separation case may occur more particularly in the examination of by-products such as anode muds.

(*a*) The fine powder is fused with potassium hydroxide and nitrate in a silver crucible (19), the cake dissolved in hot water, and the suspension submitted to distillation (43 or 44) for the determination of ruthenium and osmium. The residual solution is boiled with potassium hydroxide and alcohol (43, *β*), the precipitate containing the other platinum metals. The filtrate, containing potassium arsenate, antimonate, selenate, and tellurate, is treated as under **XIX,** § III, *e*.

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[1] W. H. Swanger and E. Wichers, *J. Amer. Chem. Soc.*, 1924, **46**, 1814.

(*β*) The fine powder is placed in a porcelain boat and heated in a current of dry chlorine (**XIX,** § III, *k*). The fixed residue in the boat is reduced in a current of hydrogen (13).

(*γ*) Cupellation with excess of silver (4) after scorification of the lead button may be used to eliminate the base metals.

(40) *From Iron, Nickel, Zinc, and Base Metals not Precipitated by Zinc or Hydrogen Sulphide.*—(*a*) *The platinum metals are present in minute quantities.* In this case the separation resolves itself into a crucible fusion with litharge and reducing fluxes (scorification optional), and cupellation of the lead button with a suitable excess of silver (4).

(*β*) *The platinum metals are present in substantial amounts.* Osmium and ruthenium, being separable by distillation, need not be considered here. The separation of the other four platinum metals from base metals is effected by the procedures given *below*.

(*γ*) Ammonium-chloride precipitation is the cleanest separation method for substantial quantities of iridium or platinum, or both, especially from much iron.[1] The acid chloride solution free from nitric acid is precipitated with ammonium chloride as prescribed under (10). The coprecipitation of iron, etc. is of the order of 0·001 to 0·002 g., and is effectively counteracted by retreatment of the precipitate (11).

(*δ*) Zinc precipitation (15) is not applicable to solutions containing iridium.

(*ε*) Hydrogen-sulphide precipitation (14) works best in the case of palladium, for which, however, dimethylglyoxime precipitation (46, *a*) is a more attractive procedure (this latter is not applicable to sulphate solutions).

(*ζ*) Titanous-sulphate precipitation (17) may be used for rhodium, palladium, and platinum.

(*η*) The nitrite process is satisfactory if the base-metal precipitate is not too bulky, and palladium quite subordinate (16).

### C. Resolution of the Platinum Group into Subgroups.

(41) *Reactions of the Platinum Metals Utilized in their Separation from One Another.*—The following differences in the chemical behaviour of the platinum metals and their principal compounds are utilized for their separation from one another:

(*a*) Fusion of the platinum metals with excess of lead at 1000° C. converts platinum, palladium, and rhodium into an acid-soluble form, while iridium, ruthenium, and osmium remain in an acid-insoluble form (45).

(*β*) Osmium and ruthenium are characterized by the ready volatility of their tetroxides (*q.v.*, § II, 1, *a* and 2, *a*). This permits of their quantitative separation from the remaining four platinum metals (and all other metals in general) by distillation. This operation is often preceded by a fusion with an alkaline oxidizing flux (18 and 19).

(*γ*) Fusion with lead, and fusion with alkali followed by distillation are the two fundamental operations in the analysis of the platinum group. Either operation brings about a subdivision of the six metals into two subgroups:

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[1] W. R. Schoeller, *Analyst*, 1926, **51**, 392.

$$\text{Lead fusion} \begin{cases} \text{Insoluble: Ru, Os, Ir.} \\ \text{Soluble: Rh, Pd, Pt.} \end{cases}$$

$$\text{Distillation} \begin{cases} \text{Volatile: Ru, Os.} \\ \text{Fixed: Rh, Pd, Ir, Pt.} \end{cases}$$

The order in which the two operations are applied is as follows:

If osmium is present in substantial quantity and the rhodium content is small, fusion and distillation should be carried out first, which leads to the following grouping:

$$\overbrace{\text{Ru, Os.} \qquad\qquad \text{Rh, Pd, Ir, Pt:}}^{\text{(i) Distillation}}$$

$$\overbrace{\text{Ir.} \qquad\qquad \text{Rh, Pd, Pt.}}^{\text{(ii) Lead Fusion}}$$

If, on the other hand, the osmium content is small and the rhodium content appreciable, the order is inverted:

$$\overbrace{\text{Ru, Os, Ir:} \qquad\qquad \text{Rh, Pd, Pt.}}^{\text{(i) Lead Fusion}}$$

$$\overbrace{\text{Ru, Os.} \qquad\qquad \text{Ir.}}^{\text{(ii) Distillation}}$$

The resolution of the above subgroups into their elements will now be considered:

(δ) Osmium tetroxide is much more stable than ruthenium tetroxide: the former is not affected by hot hydrochloric acid (1 : 1), whereas the latter is converted into non-volatile ruthenium trichloride:

$$2RuO_4 + 16HCl = 2RuCl_3 + 5Cl_2 + 8H_2O.$$

Osmium is volatilized as tetroxide when its solutions are boiled with nitric acid (distinction from ruthenium).

The following reactions are available for the separation of rhodium, palladium, iridium, and platinum:

(ε) Only palladium is precipitated by dimethylglyoxime from acid solution.

(ζ) Iridium, rhodium, and palladium can be separated from platinum by hydrolytic precipitation from neutral chloride solution in presence of sodium bromate.

(η) Rhodium, palladium, and platinum are more reducible than iridium, being precipitated as metals by titanous salt solutions; iridium tetrachloride is reduced only to the trichloride.

(θ) Ammonium chloride precipitates quadrivalent platinum, iridium, and palladium. Quadrivalent platinum and iridium are separable from bivalent palladium and from subordinate amounts of rhodium by a judicious application of this procedure.

(42) *Osmium from the Other Platinum Metals* (*and All Elements in General*).—The soluble compounds of osmium are converted into volatile osmium tetroxide when their solutions are boiled with excess of nitric acid; this property allows osmium to be quantitatively separated from all other elements by distillation.

The apparatus used consists of the distillation train connected with the osmium train (20). The amount of sodium hydroxide in the first receiver should be more than sufficient to neutralize the excess of nitric acid used in the distillation.

The osmium solution—which in practice is normally derived from a fusion with oxidizing alkaline fluxes (18, 19)—is transferred to the distillation flask, the train is connected together, and a slow current of air is passed through with the aid of the pump. Nitric acid (1 : 1) is gradually admitted into the distillation flask through a funnel connected to the inlet tube, the quantity being adjusted to about 40 ml. over and above that required to neutralize the alkali. The funnel is then disconnected and the flask gently heated while a moderate current of air is continually passing through the train. When the boiling-point is reached, the bulk of the osmium tetroxide readily distils, the colourless crystals transiently depositing in the receiver tube if much osmium is present. As the first portion of distillate mingles with the alkaline solution, it produces an orange coloration which soon changes to mauve (sodium osmate). The distillation is continued until one-half of the liquid has passed into the receiver. If no chlorides are present in the solution, the osmium should be quantitatively recovered in the distillate. To test for complete volatilization, the liquid in the distillation flask is allowed to cool, another receiver containing fresh alcoholic lye substituted for the first, and the distillation resumed. The coloration produced by the first portion of distillate in the receiver (*above*) is a sensitive indication of the presence of osmium. This is recovered from the distillates as explained in § IV, (58).

Nitric-acid distillation of osmium from acid chloride solutions is very protracted and apt to be incomplete. There is also a risk of partly volatilizing ruthenium. Such solutions are best treated as under (43).

(43) *Osmium and Ruthenium from the Other Platinum Metals* (*and All Elements in General*) *: Distillation in a Chlorine Current.*—The classic method devised by H. Ste. C. Deville and J. S. Stas[1] for the determination of ruthenium in the platinum used for the preparation of the Paris standard metre bar has undergone various modifications, thanks to which it can be applied to the separation of osmium and ruthenium from one another and from all other elements. The train used by us in upwards of 2000 operations is described under (20).

The solution under treatment (200 to 400 ml.) is usually alkaline (*i.e.* obtained from an alkaline melt: 18 or 19); if acid, it should be treated with 20 per cent. caustic soda solution representing an excess of 10 to 20 g. of sodium hydroxide. The cold solution is digested overnight in the distillation flask with at least 50 ml. of concentrated electrolytic sodium hypochlorite solution, which extracts osmium and ruthenium from the precipitated hydroxides by converting them into soluble sodium salts.

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[1] *De l'Analyse du Platine iridié*, Paris, 1878.

The complete distillation train having been connected together, a moderate current of chlorine is introduced into the distillation flask at ordinary temperature until the liquid is saturated with chlorine and the space above the liquid is filled with yellow gas. The speed of the chlorine current is then reduced to less than a bubble per second, and the contents of the distillation flask are gradually heated to boiling. If ruthenium is present in appreciable quantity, orange-yellow vapours of the tetroxide are evolved, and yellow crystals deposit in the inlet tube of the receiver until fused and carried down by the rush of steam. The acid in the first receiver acquires a yellow colour, which soon turns a deep reddish-brown as the bulk of the ruthenium tetroxide becomes converted into trichloride by the hot acid. When the steam no longer condenses, but bubbles through the liquid in the first receiver, this is heated by the Bunsen flame, the tip of which should just touch the wire gauze supporting the flask. The osmium, and still unreduced ruthenium, tetroxides are thus driven into the second receiver, where a further quantity of the latter is reduced to trichloride as the liquid becomes hot. When boiling-point has been reached in the second receiver, this is heated in its turn with a moderate flame, the osmium and a small quantity of ruthenium reaching the third receiver, which is treated exactly like the second. The chlorine supply is meanwhile disconnected and replaced by a moderate air current through the suction pump. With the four burners alight and a lively current of steam bubbling through the fourth receiver, the distillation is continued for some time, during which the osmium is absorbed in the fifth receiver, imparting a more or less intense mauve colour to the contents. The acid liquid in the small receiver (No. 4) should remain colourless or show only a faint brown tinge, proving that the whole of the ruthenium has been absorbed in Nos. 1 to 3. When complete absorption of the osmium in No. 5 has apparently taken place, the distillation is continued for another 15 to 20 minutes, the total time taken amounting to about one and a half hours. While the air current is still passing through the train, the four burners are turned off, the distillation flask is disconnected, No. 4 receiver from No. 5 next, and finally No. 6 from the pump.

The recovery of the osmium is normally complete in one operation; the osmate solution from the two receivers is transferred to a capacious beaker, and the osmium determined as described in § IV, (58) or (59).

The ruthenium recovery, on the other hand, is usually incomplete, due to partial decomposition of the tetroxide in the distillation flask. The contents of the receivers Nos. 1 to 4, forming the major ruthenium fraction, are transferred to a 600-ml. beaker and evaporated to dryness on a water-bath (see § IV, 60).

For the recovery of the minor ruthenium fraction, a second distillation is necessary.

(*a*) The simplest process of general applicability consists in cooling the liquid in the distillation flask to room temperature, treating it with 50 ml. of electrolytic hypochlorite solution to which a cold strong solution of 10 g. of sodium hydroxide has been added, and again setting it aside overnight. Next morning another 20 ml. of hypochlorite solution is added prior to chlorine distillation in a train consisting of the distillation flask and the ruthenium receivers Nos. 1 to 3 containing dilute hydrochloric acid as in the major distillation. A chlorine absorption flask containing caustic soda is inserted between No. 3 receiver and the suction pump. The distillation is carried out as described *above*, the contents of the receivers being added to the beaker containing the major fraction.

The residual solution from the single or double distillation is worked up as described under ($\beta$), *below*.

($\beta$) The recovery of the minor ruthenium fraction may be conveniently combined with the separation of iridium from the other platinum metals by the lead fusion method. The sequence of manipulations is as follows: precipitation of the metals from the residual solution of the osmium-ruthenium distillation by boiling with sodium hydroxide and alcohol; solution of the precipitate in *aqua regia*, and recovery of a minute quantity of iridium (in crucible *A*) from the separated silica (21); precipitation of the filtrate with ammonium chloride in two fractions, $P^1$ and $P^{1a}$ (10), which are added to crucible *A*, ignited, and reduced (12 and 13); and precipitation of the filtrate from $P^{1a}$ with zinc (15).

The total platinum metals are contained in the ignited and reduced ammonium-chloride and zinc precipitates, the minor ruthenium fraction being distributed between the two. The combined precipitates are fused with lead (3), the lead button is treated as under (2), and the insoluble iridium-ruthenium alloy is collected, washed, ignited, reduced, and weighed as Ir + Ru. It is then fused with sodium peroxide (18), and the solution of the melt submitted to distillation, the apparatus consisting of distillation train and ruthenium train. The bromate process (44) may be used; the minor ruthenium fraction is determined separately (§ IV, 60), iridium being computed by difference.

If the chlorine distillation method is used, the completeness of the ruthenium recovery may be tested by a third distillation, as under ($a$), *above*. The quantity thus obtained normally amounts to less than 0·001 g.

(44) *Osmium-Ruthenium Distillation with Bromate.*—In this more recently introduced method, the distillation train is exactly the same as that used in (43), including a gas-washing bottle before the distillation flask for gauging the speed of the air current circulating through the system. The alkaline solution is digested with hypochlorite in the distillation flask overnight as before. The train is connected up, and a slow current of air drawn through it. The solution is then raised to the boiling-point, and the gas-washing bottle replaced by a glass tube, through which hydrochloric acid is cautiously aspirated from a beaker until the black precipitate has dissolved. The clear, boiling solution is next treated with 25 per cent. sodium chlorate solution (10 to 20 ml.) introduced through the tube, when the tetroxides of osmium and ruthenium distil into the first receiver. The volatile compounds are then driven gradually through the ruthenium receivers, the burners being lit in succession as detailed under (43).

When no further darkening of the reddish-brown colour can be observed in the contents of the ruthenium receivers, 10 to 20 ml. of bromate-bromide solution (120 g. of sodium bromide and 36 g. of sodium bromate made up with water to 1 litre) is aspirated into the distillation flask, and the distillation is continued for 10 to 15 minutes after the evolution of bromine has ceased, when it is interrupted as under (43); if iridium is present, incipient precipitation of its hydroxide should take place towards the end of the distillation. The recovery of osmium and ruthenium is quantitative in one operation.

(45) *Iridium, Ruthenium, and Osmium from Platinum, Rhodium, and Palladium: Lead Fusion Method.*[1]—The lead alloy is obtained either by crucible fusion of ores, etc. with litharge and fluxes or by fusion of the spongy platinum metals with lead in a carbon crucible (3). The importance of this procedure in conjunction with peroxide fusion and distillation is discussed under (41, $\gamma$). It must be understood that, if osmium is present in substantial amounts, fusion with alkali and distillation should always precede fusion with lead.

(46) *Palladium from Platinum, Iridium, and Rhodium.*—Precipitation of the palladium with dimethylglyoxime, being a convenient and accurate process, has displaced the older cyanide and iodide procedures.

(*a*) *Precipitation with dimethylglyoxime.*[2] The moderately acid chloride solution is diluted to 200 ml., treated with a slight excess of a 1 per cent. solution of the reagent in 2 per cent. hydrochloric acid (0·1 g. of palladium requires 0·22 g. of precipitant), and set aside for half an hour. The bulky, orange-yellow precipitate is collected and washed with 1 per cent. hydrochloric acid, then with hot water (further treatment: see § IV, 68).

The precipitation of palladium from sulphate solutions is not quite quantitative.

The above process separates palladium from all metals except gold, which is quantitatively precipitated. It may, therefore, be recovered from the solution with the palladium. In this case the washed precipitate is rinsed back into the beaker, and the suspension boiled with dilute *aqua regia* until the precipitate has dissolved. The solution is cooled, diluted until the acidity is reduced to 2 to 3 per cent., and the palladium reprecipitated with dimethylglyoxime [3]: the nitric acid present in the solution prevents the coprecipitation of the gold. For the same reason, palladium alone will be precipitated if nitric acid is present in, or is added to, the original solution.

Platinum is coprecipitated to a certain extent with the palladium if the solution is hot and an alcoholic solution of the reagent is employed, part of the platinum being reduced to the platinous condition, in which it reacts like palladium. The coprecipitation of platinum is detected by the greenish tint of the palladium precipitate, and is prevented by working in cold dilute solution as prescribed *above*, or by addition of nitric acid. Platiniferous palladium precipitates may be purified, as may those containing gold (*above*), by reprecipitation from dilute *aqua regia* solution.

The filtrate from the palladium precipitate is freed from excess of precipitant by evaporation almost to dryness and digestion with sodium chlorate and hydrochloric acid.

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[1] H. Ste. C. Deville and J. S. Stas, *op. cit.*

[2] M. Wunder and V. Thüringer, *Zeitsch. anal. Chem.*, 1913, **52**, 101.

[3] *Ausgew. Methoden*, p. 137.

The palladium precipitate being very voluminous, suction filtration should be employed for quantities of metal exceeding 0·05 g. It may be advisable to dissolve larger precipitates in *aqua regia* and repeat the precipitation. In the case of very large quantities of palladium the bulk of the metal may be precipitated as iodide (*β*, *below*) and the balance with dimethylglyoxime (see also § IV, 69).

(*β*) *Precipitation as iodide.* The black precipitate of palladous iodide being soluble in excess of potassium iodide (§ II, *g*), the quantitative precipitation of soluble iodides by excess of palladous salt is a much simpler operation than that of palladium by an iodide. A dilute palladous nitrate solution free from alkali salt is precipitated completely by hydriodic acid added in very slight excess, but this procedure is almost devoid of practical interest. The use of potassium iodide as a reagent for palladium is now confined to the analysis of the commercial metal, in which the bulk of the palladium is eliminated by precipitation with a calculated amount of the reagent (§ VIII, 95).

(*γ*) *Precipitation as cyanide.* This procedure separates palladium from the other platinum metals; but it is probably only of historic interest. The acid nitrate or sulphate, or neutralized chloride, solution is treated with excess of mercuric cyanide solution, and the liquid gently warmed until the free hydrocyanic acid is expelled and the precipitate has settled. The precipitate is collected, washed, dried, ignited, reduced, and weighed as metallic palladium.

(47) *Platinum from Iridium, Rhodium, and Palladium: Bromate Hydrolysis.*[1]—The chloride solution, freed from excess of acid by evaporation, is diluted to 200 to 300 ml., boiled, and treated with 20 ml. of 10 per cent. sodium bromate solution, followed by a 10 per cent. solution of sodium bicarbonate added drop by drop until the dark green solution shows signs of cloudiness. The acidity must be carefully adjusted by means of a 0·01 per cent. solution of bromcresol purple while the neutralization proceeds. A drop of the indicator is allowed to run down the glass rod used for stirring the solution so as to mingle with the drop of liquid at the tip of the rod; a colour change from yellow to blue shows that sufficient bicarbonate has been added. After addition of another 10 ml. of bromate solution, the liquid is boiled for 5 minutes; more bicarbonate solution is then added drop by drop, the reaction being determined as before, but with a drop of a 0·01 per cent. solution of cresol red. When this produces a faint pink colour in the test drop, a further 10 ml. of bromate solution is added, and the solution boiled for 15 minutes. The flocculent precipitate (hydroxides of iridium, rhodium, and palladium) is allowed to settle, collected in a glass filtering crucible, and washed with hot 1 per cent. sodium chloride solution. Crucible and precipitate are returned to the beaker, 10 to 20 ml. of strong hydrochloric acid is poured into the crucible, and the covered beaker is heated on the water-bath until the precipitate has dissolved. The crucible is then rinsed with water, transferred to a small beaker, and treated twice with

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[1] R. Gilchrist and E. Wichers, *J. Amer. Chem. Soc.*, 1935, **57**, 2565.

5-ml. portions of strong hydrochloric acid on the water-bath for the purpose of extracting the chlorides from the porous bottom. The extracts are added to the bulk; the solution is evaporated to dryness with 2 g. of sodium chloride, the residue dissolved in 300 ml. of water, and the whole of the above operations are repeated.

The two filtrates containing the platinum are treated separately with hydrochloric acid to decompose the bromate, concentrated by evaporation, combined, and evaporated to dryness. The residue is taken up with hot water, the solution filtered, and the filter washed with 1 per cent. hydrochloric acid. The filtrate is acidified with 5 per cent. by volume of hydrochloric acid, heated, and precipitated with a rapid stream of hydrogen sulphide until cold. The precipitated platinum sulphide is collected, washed with 1 per cent. hydrochloric acid, dried, and ignited in a porcelain crucible. The ignited metal is leached with dilute hydrochloric acid, again ignited, and weighed. It retains on the average 0·0005 g. of sulphur, which cannot be expelled by ignition in air or in hydrogen.

The precipitated hydroxides of iridium, etc. are dissolved in strong hydrochloric acid as before, and the palladium is precipitated as under (46, *a*). The filtrate is evaporated with nitric and 10 ml. of sulphuric acid until it fumes strongly; after dilution, rhodium is separated from iridium by double precipitation with titanous sulphate (48).

(48) *Iridium from Rhodium, Palladium, and Platinum: Titanous Sulphate Method.*[1]—The principle of this method and the procedure have been given under (17). Gilchrist and Wichers apply this method to the separation of iridium from rhodium. They collect the precipitated rhodium on a paper filter, wash it with 5 per cent. sulphuric acid, return it to the beaker together with the paper, and destroy the paper with nitric and sulphuric acids. After complete elimination of the nitric acid the precipitation with titanous salt is repeated. The rhodium (which contains a little titania) is dissolved as before, the sulphate solution boiled with hydrochloric acid, and the hot solution treated with a rapid stream of hydrogen sulphide till cold. The precipitated rhodium sulphide is collected, washed with dilute sulphuric and finally with 1 per cent. hydrochloric acid, ignited in a porcelain crucible, reduced, and weighed as rhodium.

The drawback of this method consists in the interference of titanium with the iridium determination. Gilchrist and Wichers find it necessary to precipitate the titanium from the combined iridium filtrates by means of cupferron (**XIII**, § III, *e*). The cupferron precipitate is boiled with nitric and sulphuric acids, the resultant solution (freed from nitric acid) is re-precipitated with cupferron, and the combined filtrates are boiled down until 10 ml. of sulphuric acid remains. The iridium in the residual liquid is precipitated by hydrolysis with sodium bicarbonate and bromate as described under (47), and the iridium hydroxide converted into and weighed as metallic iridium (§ IV, 66).

We give preference to the lead fusion process (45) over the titanous sulphate method as the regular procedure for the separation of iridium from platinum, palladium, and rhodium. Precipitation by titanous sulphate is most useful in the separation of small quantities of platinum, palladium, and especially rhodium, from preponderating amounts of iridium when there is no need to recover and determine that element (*e.g.* in the analysis of iridium). The small precipitate produced by titanous salt is ignited, reduced, weighed, and fused with sodium chloride in a current of chlorine (22). The melt is dissolved in a little water, any coprecipitated titania remaining insoluble. If only rhodium is present, the aqueous extract is of a pure rose-red colour; in the presence of platinum or palladium or both, the procedure given under (50) should be applied.

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[1] After R. Gilchrist and E. Wichers (*loc. cit.*), who use titanous chloride.

(49) *Platinum and Iridium from Small Quantities of Palladium and Rhodium: Ammonium Chloride Method.*—This is the oldest procedure for the joint precipitation of platinum and iridium from chloride solutions containing subordinate amounts of palladium and rhodium, as well as base metals (*e.g.* the solution obtained by the action of *aqua regia* upon native platinum, or upon the hydroxide precipitate obtained after distillation in osmiridium analysis). The method was for a long time held to effect a quantitative separation of platinum and iridium from palladium and rhodium in a single precipitation, but such is not the case. The precipitate occludes part of the palladium and rhodium, from which it can be freed by recrystallization. The primary precipitate, $P^1$, obtained as under (10), is purified by the chlorine process (11), yielding the pure precipitate, $P^2$. The combined filtrates from $P^1$ and $P^2$ are worked up for the minor fraction $P^{1a}$ (10 and 11). This small dark precipitate contains the balance of the platinum and iridium and, generally, a little palladium. It is collected, washed with ammonium chloride solution, strongly ignited, reduced, and extracted with *aqua regia* (1 : 3 water). The insoluble residue (a little iridium) is collected, washed, and added to $P^2$, which is cautiously ignited (12), reduced, and weighed as Pt (major fraction) + Ir (further treatment: see 54).

The filtrate from the extraction of the ignited $P^{1a}$, containing the minor platinum fraction, is evaporated to dryness, then twice with hydrochloric acid, the residue taken up with a little 5 per cent. hydrochloric acid, and the solution precipitated with ammonium chloride. The precipitate, $P^{2a}$, is ignited to platinum; it is not so pure as $P^2$, but, being small, its weight after ignition can be added to that of the major fraction without causing an appreciable error.

The combined filtrates from $P^{1a}$ and $P^{2a}$ contain the palladium and rhodium, which are separated from base metals by precipitation with zinc (15), then from one another as under (50), *below*. If it is desired to test the zinc precipitate for platinum, it is digested with hot dilute *aqua regia* (1 : 7 water), the insoluble part of the rhodium, if any, filtered off, and the filtrate evaporated and treated exactly as that from the extraction of the ignited $P^{1a}$. The precipitate, if any, is so small that no appreciable error is incurred by addition of its weight, even if only 90 per cent. pure, to the platinum result.

(50) *Rhodium from Platinum and Palladium.*—The procedure is carried out in chloride solution. If the metals have been precipitated by zinc (15), titanous sulphate (17), or hydrazine (34), the filter containing the metallic sponge is washed with 1 per cent. hydrochloric acid, returned to the beaker,

and boiled with dilute *aqua regia* (1 : 3 water). The pulped filter, containing part of the rhodium free from platinum and palladium (*cf.* 33), is collected, well washed, ignited, and reserved (insoluble rhodium fraction). The filtrate is treated with dimethylglyoxime (46, α); the precipitate contains the whole of the palladium.

The filtrate from the palladium precipitate is evaporated to dryness and the residue taken up with strong hydrochloric acid, which is again evaporated, with the addition of small amounts of sodium chlorate for the destruction of the dimethylglyoxime. The final residue is taken up with hot water and a drop of hydrochloric acid, and the soluble rhodium fraction is separated from platinum by bromate hydrolysis (53, δ).

## D. Separation of Binary Mixtures of the Platinum Metals.

The distillation methods (42 to 44) given under C are applied whenever osmium, or ruthenium, or both, have to be separated from one or more of the other four platinum metals. What remains to be discussed in the following paragraphs is the separation of pairs or binary mixtures of these elements into their constituents.[1] Since most of the separation procedures have already been described, it will be sufficient in the majority of cases to refer back to C.

(51) *Osmium from Ruthenium.*—(α) The most convenient procedure, which has the great advantage of effecting the simultaneous separation of osmium from ruthenium, and of both from all other elements, has been described under (43) and (44).

(β) Osmium may also be separated from ruthenium by distillation with nitric acid (42).

(52) *Platinum from Palladium.*—(α) Palladium is precipitated by dimethylglyoxime (46, α), or, if in very large excess (as in the analysis of palladium), by a deficiency of potassium iodide supplemented by dimethylglyoxime (§ VIII, 95).

(β) Platinum is precipitated with ammonium chloride, the primary chloroplatinate precipitate being retreated by the chlorine process (10 and 11; 49). The separation method favoured by Krauss and Deneke [2] is evaporation to dryness of the chloride solution, free from nitric acid, with a slight excess of ammonium chloride (*i.e.* the procedure employed in the chlorine process), and treatment of the residue with water and saturated ammonium chloride solution.

(53) *Platinum from Rhodium.*—(α) The separation of the finely divided ignited metals by fusion with bisulphate is unreliable, the platinum residue retaining rhodium even after several repetitions of the procedure.

(β) Precipitation of platinum with ammonium chloride (10) and purification of the chloroplatinate precipitate as under (11), when applied in the analysis of native platinum (maximum rhodium : platinum ratio observed, 0·014) gives a final platinum-iridium precipitate in which no weighable amount of rhodium can be detected.[3]

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[1] The number of possible pairs of $n$ elements is $n(n-1)/2$.

[2] F. Krauss and H. Deneke, *Zeitsch. anal. Chem.*, 1925, **67**, 86.

[3] W. R. Schoeller, *Analyst*, 1930, **55**, 550.

(γ) *Barium carbonate method.*[1] This method is based, as is that given *below*, upon the hydrolytic precipitation of rhodium hydroxide in boiling neutral or faintly alkaline solution. The precipitate must be retreated, and if more than 1 per cent. of rhodium is present a third precipitation may be necessary. The procedure is much less convenient than bromate hydrolysis (δ), hence it need not be described here.

(δ) *Bromate hydrolysis.* Procedures for separating rhodium from platinum by bromate hydrolysis have been published by Moser and Graber,[2] and Gilchrist and Wichers (47). We have applied bromate-bromide hydrolysis to this separation for over 12 years.

The neutral chloride solution (acid solutions should be neutralized with sodium carbonate), containing normally an excess of platinum over rhodium, is diluted considerably (to 300 to 500 ml.), heated to boiling, and treated with a solution containing 30 g. of sodium bromate and 100 g. of sodium bromide per litre, the rhodium being gradually precipitated as dark green hydroxide, with evolution of bromine. Boiling is continued for some time until the precipitate flocculates, more reagent being added and the effect noted. There should be no further evolution of bromine upon addition of reagent.

The liquid is treated with 2 per cent. sodium bicarbonate solution until neutral to bromcresol purple, and set aside on the water-bath until the precipitate has settled. This is collected, washed with 2 per cent. sodium chloride solution, dissolved in hydrochloric acid, and the precipitation repeated. If small amounts of rhodium and platinum are involved, a single precipitation may suffice.

The filtrate from the rhodium precipitate should always be tested for complete precipitation by renewed boiling with bromate reagent. If very little rhodium is present, the filtrate should be tested by boiling with a few drops of sodium bicarbonate solution, which precipitates the last of the rhodium.

The rhodium hydroxide is returned to the beaker with hot water, the filter cleaned with a little hydrochloric acid, and the rhodium reduced to metal by boiling with a slight excess of sodium carbonate and hydrazine salt solution (§ IV, 72).

The platinum filtrate is cautiously freed from excess reagent by boiling with hydrochloric acid, concentrated by evaporation, neutralized with sodium carbonate, and precipitated with hydrazine (§ IV, 63).

(54) *Platinum from Iridium.*—Two accurate methods are available for this separation:

(α) The lead fusion method of Deville and Stas (45), which was fully re-investigated by R. Gilchrist.[3] It was confirmed that palladium and rhodium do not interfere with the iridium determination, but ruthenium remains quantitatively with the iridium, and iron nearly so.

(β) Bromate hydrolysis, first described by Moser and Hackhofer,[4] and modified by Gilchrist and Wichers (47).

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[1] E. Wichers, *J. Amer. Chem. Soc.*, 1924, **46**, 1818.
[2] L. Moser and H. Graber, *Monatsh.*, 1932, **59**, 61.
[3] *Sci. Papers Bur. Stand.*, 1924, **19**, 325.
[4] L. Moser and H. Hackhofer, *Monatsh.*, 1932, **59**, 44.

(55) *Palladium from Rhodium.*—Palladium is precipitated from slightly acid chloride solution by dimethylglyoxime (46, *a*); see also (34).

(56) *Palladium from Iridium.*—The separation may be effected by the following methods:

(*a*) Fusion with lead (45).

(*β*) Precipitation of the palladium with dimethylglyoxime (46, *a*).

(*γ*) See also (49) for the deportment of palladium and iridium in the ammonium chloride method.

(57) *Rhodium from Iridium.*—(*a*) As in the case of the separation of rhodium from platinum (53), fusion with bisulphate is ineffective.

(*β*) Fusion with lead (45) is a serviceable method, and the only one available for the determination of iridium (ruthenium) in compact or granulated rhodium. If the rhodium : iridium ratio is high, it is advisable to submit the iridium residue from the acid extraction of the lead button to a second fusion with lead and to repeat the whole process.

(*γ*) Small quantities of rhodium are separable from iridium by precipitation of the latter with ammonium chloride and purification of the chloriridate precipitate (49).

(*δ*) Precipitation of the rhodium with titanous salt has been described under (48).

§ **IV. Gravimetric Determination.**—In nearly every case, the platinum metals are determined gravimetrically, being weighed as such after having been precipitated in the metallic state or in the form of some compound (*e.g.* sulphide, hydroxide, " double " chloride). The determination of osmium differs from that of the other five members of the group in that its precipitates must be ignited with the exclusion of air, as otherwise the metal is completely volatilized as tetroxide.

Ruthenium, rhodium, palladium, and iridium precipitates yield an ignition residue consisting either wholly or partly of oxide, which must be reduced to metal by gentle ignition in hydrogen (13); and since a certain amount of that gas may be superficially absorbed by the reduced metal and catalytically oxidized to water on subsequent contact with the air, with attendant risk of positive errors, the hydrogen is displaced during cooling by carbon dioxide.

Platinum is the " noblest " of the six metals, its precipitates being converted into metal by simple ignition in air. Even so, it is prudent to reduce large platinum precipitates in the manner described *above.*

(58) *Osmium: Precipitation as Hydroxide.*[1]—The gravimetric determination of osmium is always preceded by its precipitation either as hydroxide or as sulphide from an alkaline solution of sodium osmate (obtained as under 42, 43, or 44). If the amount of osmium to be determined is substantial (as indicated by the more or less intense mauve colour of the osmate solution) it should be precipitated as hydroxide; if, on the other hand, the solution is barely or faintly coloured, precipitation as sulphide (59, *below*) is to be preferred.

For the precipitation as hydroxide, the alkaline osmate solution is transferred from the receiver to an 800-ml. beaker, and approximately neutralized with sulphuric acid (1 : 1), the colour of the solution turning from mauve to brown (about 20 ml. of acid are required for an initial charge of 25 g. of sodium hydroxide). The solution is then heated to about 60° C., accurately neutralized with 2N. sulphuric acid (spot test on litmus-paper), and gently boiled for some hours or until the deep black pulverulent precipitate of osmium hydroxide settles readily. Ruff and Bornemann use phenolphthalein as internal indicator, heating the solution with occasional additions of dilute sulphuric acid until the colour of the indicator is permanently discharged. After having been set aside overnight the precipitate is collected in a porous porcelain filtration crucible, and thoroughly washed with saturated ammonium chloride solution; the crucible is allowed to dry over sulphuric acid, placed inside a Vitreosil Rose crucible, and warmed with a micro-burner in a stream of dry hydrogen, reduction to metal taking place below 200° C., frequently attended with slight decrepitation. If this becomes at all pronounced the flame should be at once withdrawn. Once started, the reduction proceeds readily, the ammonium chloride from the wash-liquor lessening decrepitation. The heat is gradually increased, the Rose crucible being finally heated with the full flame of a Bunsen burner for half an hour. The reduced osmium is allowed to cool under hydrogen, which is then displaced by dry carbon dioxide. Any small black particles projected into the outer crucible during decrepitation are brushed into the porous crucible, which is weighed, and then heated in an efficient draught-cupboard until the osmium has been volatilized. The crucible is ignited to constant weight, which is more readily attained if towards the end of the operation a luminous Bunsen flame is directed from time to time into the inclined crucible. The weight of the fixed residue (consisting of silica derived from the action of the alkali on the beaker) is subtracted from the first weight, the difference being the weight of the osmium.

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[1] After O. Ruff and F. Bornemann, *Zeitsch. anorg. Chem.*, 1910, **65**, 429.

(59) *Osmium: Precipitation as Sulphide.*—The alkaline osmate solution is heated with ammonium polysulphide, boiled for 10 to 15 minutes, and acidified with hydrochloric acid. After slight cooling, it is treated with a moderate excess of ammonia and more polysulphide, again boiled for 10 minutes, re-acidified, and finally boiled until the sulphur coagulates. The precipitate is collected in a porous porcelain crucible, and washed, ignited under hydrogen, etc. exactly as described for the hydroxide precipitate (58, *above*), including the determination of osmium by difference. The results obtained by this method have a tendency to be slightly high, since osmium obtained by ignition of the sulphide in hydrogen generally retains a little sulphur, which is volatilized with the metal during subsequent ignition. The procedure should be applied only to small amounts of osmium.

(60) *Ruthenium: Precipitation as Sulphide.*—The determination of ruthenium is always preceded by a distillation, the ruthenium being obtained as chloride in the distillate (43 or 44). The solution is freed from excess of acid by evaporation on the water-bath almost to dryness, and the residue dissolved in 100 to 200 ml. of 2 per cent. hydrochloric acid. The solution is boiled with excess of ammonia and ammonium polysulphide for 10 minutes, acidified with dilute hydrochloric acid, and boiled for some time until the mixed precipitate of sulphur and ruthenium sulphide coagulates completely.

The precipitate is collected, washed with hot water, ignited wet in a tared crucible, reduced as usual (13), and weighed as ruthenium.

(61) *Ruthenium: Combination Process.*—If large quantities of ruthenium (*e.g.* more than 0·2 g.) have to be determined, the preceding method (60) becomes inconvenient on account of the bulkiness of the precipitate. In such cases the bulk of the ruthenium may be precipitated from the concentrated distillate by addition of solid ammonium chloride until the liquid is saturated. The brown crystalline precipitate (ammonium chlororuthenite) is collected, washed twice with ammonium chloride solution, and ignited with the usual precautions (12). The pale brown filtrate and washings are precipitated with polysulphide as under (60), *above*, the balance of the ruthenium being recovered as sulphide. The double-chloride precipitate is crystalline and compact, but comparatively soluble, hence the necessity for a combination process.

(62) *Platinum: Precipitation as Ammonium Chloroplatinate.*—The precipitation of platinum as potassium chloroplatinate, advocated in the earlier literature, has nothing in its favour, while suffering from the double disadvantage that the precipitate cannot be ignited to metallic platinum, nor redissolved by decomposition with chlorine. The procedure has fallen into disuse.

The precipitation of ammonium chloroplatinate has been described under (10), and its ignition to metal under (12). If large, the ignited precipitate should be given a short reduction with hydrogen (13).

(63) *Platinum: Precipitation as Metal.*—The chloride solution, freed from nitric acid if necessary by double evaporation with hydrochloric acid, or from excess of hydrochloric acid by evaporation with a slight excess of sodium chloride (0·6 g. per g. of platinum), is diluted to 100 to 200 ml., neutralized with sodium carbonate solution, and boiled with a moderate excess of 10 per cent. hydrazine hydrochloride solution until the precipitated platinum has coagulated. This is left to settle, filtered by decantation, washed several times with hot water, and digested with hot 1 per cent. hydrochloric acid, which removes any adsorbed alkali. The precipitate is collected, washed with acidulated water, ignited, and reduced if bulky (*cf.* 62).

(64) *Platinum: Precipitation as Sulphide.*—Gilchrist and Wichers [1] dilute the chloride solution to 400 ml., add 5 ml. of hydrochloric acid per 100 ml., and treat the hot solution with a rapid stream of hydrogen sulphide, the treatment being continued while the liquid cools. The precipitate is collected, washed with 1 per cent. hydrochloric acid, dried, and ignited in a porcelain crucible. The resultant metal is leached with dilute hydrochloric acid, again collected, strongly ignited, and weighed. The metal thus obtained contains on an average 0·0005 g. of sulphur per gram (*cf.* osmium, 59) which cannot be expelled by ignition.

(65) *Iridium: Precipitation as Ammonium Chloriridate.*—What has been said under (62) regarding the precipitation of potassium chloroplatinate applies equally to iridium. The procedure for the precipitation of ammonium chloriridate has been given under (10). Chloriridic acid being more readily reducible than the platinum derivative, the filtrate from the precipitate

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[1] *Loc. cit.* (47).

produced by ammonium chloride should always be evaporated with occasional addition of a drop of sodium chlorate solution (or a small crystal of the solid salt), until ammonium chloride begins to crystallize out. After standing overnight, the solution is filtered, usually yielding a very small second crop of ammonium chloriridate. The ignited iridium must always be reduced.

(66) *Iridium: Precipitation as Hydroxide.*—This has been described under (47). The precipitate is thoroughly washed with 1 per cent. ammonium chloride solution, dried by gentle warming in a porcelain crucible, moistened with a few drops of saturated ammonium chloride solution (to prevent decrepitation), ignited very gently at first, then strongly, and reduced in hydrogen. The ignited metal is leached with dilute hydrochloric acid, again collected, ignited, reduced, and weighed.

(67) *Iridium: Precipitation as Metal.*—Iridium is precipitated as metal from chloride solution by means of hydrazine hydrochloride. The directions given under (63) for platinum are followed, with this difference, that the solution must be made alkaline, not merely neutralized, with sodium hydroxide. The unignited iridium is leached with 1 per cent. hydrochloric acid.

(68) *Palladium: Precipitation with Dimethylglyoxime.*—The precipitation, and the precautions to be observed in the presence of gold and platinum, are described under (46, *a*). The washed precipitate wrapped in the filter is transferred to a tared porcelain crucible, and gently heated on an asbestos mat till dry; the heat is then gradually increased until the paper has charred, and finally the metal is ignited more strongly, reduced in hydrogen, and cooled under carbon dioxide (13).

Alternatively, the precipitate produced by dimethylglyoxime may be collected on a tared filter or porous porcelain crucible, washed as before, and heated to constant weight at 110° C. (palladium factor: 0·3167).

(69) *Palladium: Precipitation as Ammonium Chloropalladate.*—The preceding method is impracticable for large quantities of palladium on account of the bulkiness of the precipitate. In such cases it is convenient to precipitate the palladium with ammonium chloride.[1]

The chloride solution, containing a liberal amount of ammonium chloride (*e.g.* the filtrate from an ammonium-chloroplatinate precipitation), is slowly evaporated on the water-bath with excess of nitric acid. The palladium separates as a bright red crystalline precipitate, the solution becoming colourless. After cooling, the precipitate is collected, washed with strong ammonium chloride solution, ignited gently as prescribed under (12), and reduced in hydrogen.

The filtrate from the chloropalladate precipitate should always be tested with dimethylglyoxime for the complete recovery of the palladium. A small but significant quantity of precipitate is usually obtained.

Ignited palladium, which has usually a deep purple colour due to a surface film of oxide, may be treated with a few drops of formic acid on the water-bath instead of being reduced in hydrogen. The dry residual metal is weighed.

(70) *Palladium: Precipitation as Sulphide.*—Palladium is readily pre-

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[1] P. Cohn and F. Fleissner, *Zeitsch. anal. Chem.*, 1897, **36**, 796.

cipitated by hydrogen sulphide from acid solutions, but the precipitate does not part with the whole of its sulphur on ignition, and the impure metal runs into one or several globules. The sulphide precipitate should be dissolved in *aqua regia*, and the solution treated as under (68) or (69).

(71) *Rhodium: Precipitation as Metal.*—The chloride solution is rendered alkaline with sodium carbonate, and boiled with hydrazine hydrochloride solution in excess until the precipitated metal coagulates. The procedure is the same as that for iridium (67), including lixiviation of the unignited precipitate with 1 per cent. hydrochloric acid. The precipitate is ignited in a tared porcelain crucible, reduced in hydrogen, and cooled in carbon dioxide.

(72) *Rhodium: Precipitation as Hydroxide.*—Rhodium hydroxide, precipitated by bromate hydrolysis (47 and 53, δ), is reduced to metallic rhodium by the procedure given under (71): the hydroxide precipitate is returned to the beaker and boiled with sodium carbonate and hydrazine hydrochloride solutions, etc. as *above.*

(73) *Rhodium: Precipitation with Zinc or Magnesium.*—Rhodium is quantitatively precipitated from chloride or sulphate solution by displacement with zinc or magnesium (15). The method gives high results, especially with zinc as a reductor, but is sufficiently accurate for the determination of very small amounts of rhodium in technical work. The precipitated metal is filtered off, washed with dilute hydrochloric acid, ignited, reduced, and digested with N. hydrochloric acid on a water-bath for half an hour. It is again collected, washed, ignited, and reduced.

§ V. **Volumetric and Colorimetric Determination.**—There are no reliable methods for the volumetric determination of the platinum metals. On account of the intense colour of the solutions of many compounds of these elements, their colorimetric determination appears at first sight an attractive proposition; yet, with two exceptions (74 and 75), no colorimetric method has been adopted in actual practice. For colorimetric purposes the platinum metals would first have to be quantitatively separated from one another, and once this has been done the gravimetric determination of these valuable metals is comparatively simple as well as more accurate. A serious objection against colorimetric methods is the fact that the colour is strongly influenced by a number of factors such as ageing and acid concentration. The deep reddish-brown ruthenium distillate (43), for example, turns a yellow-brown on standing, due to partial hydrolysis.

(74) *Platinum: Colorimetric Determination.*[1]—The process is based on the reduction of chloroplatinic to chloroplatinous acid by stannous chloride, the solution turning red if sufficiently concentrated, but changing to yellow upon dilution. The intensity of the colour is inversely proportional to the acidity, hence the solutions to be matched must be prepared with standardized hydrochloric acid (33 ml. of concentrated acid per litre). The method is not recommended for quantities of platinum exceeding 0·0002 g. The stannous chloride solution, containing 5 g. of the crystallized salt in 10 ml. of standard acid, should be freshly prepared.

The platinum to be determined (0·005 to 0·2 mg.) is dissolved in a few drops of *aqua regia*, the solution being evaporated. After two evaporations with hydrochloric acid, the residue is taken up with 2 ml. of standard acid.

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[1] C. W. Davis, *Tech. Paper* **270**, *U.S. Bureau of Mines*, 1921, p. 15.

A scale of standards, containing known quantities of platinum as chloroplatinic acid, is prepared by evaporation to dryness and solution of the residue in 2 ml. of standard acid. Two drops of tin solution are added, and the tints are matched in small tubes after 15 minutes' standing, when the colour has fully developed and remains unchanged for some hours. Palladium, if present, gives a deep brown colour.

(75) *Palladium: Colorimetric Determination.*[1]—Minute quantities of palladium impart a yellow colour to the nitric acid used for parting silver beads. Comparison of the tint with that of a solution of known palladium content does duty as a rapid works method in serial determinations.

§ **VI. Detection in Ores.**—(76) *Detection Combined with Determination.*—Since the detection of the platinum metals in ores, etc. follows the same lines as the quantitative determination, much time is saved by combining the two operations; in other words, the search for these metals is conducted on a weighed quantity of sample, and the various chemical or mineralogical operations are carried out quantitatively; if they give positive indications for platinum metals, a quantitative figure or, at least, a preliminary approximate value can be got by appropriate treatment, the "qualitative" test doing duty as a pilot assay.

(77) *Association of the Platinum Metals in Nature.*—The analyst searching for platinum metals in ores, alluvials, rocks, and concentrates derived therefrom, should bear in mind that these closely related elements almost invariably occur together, though some of them are usually present in much smaller proportions than the others. A positive reaction for one member of the group must therefore be taken as a fairly definite indication that others are also present. The following rules are of fairly general applicability. In base-metal ores (78), platinum and palladium are the only members likely to be detected; either may predominate. If concentrated (*e.g.* by flotation, smelting, or electrolytic processes), the material may give indications of rhodium in much smaller amounts than platinum or palladium, the remaining three metals being scarcer still. Alluvial materials, black sands, etc. (79) may contain platinum metals in the form of either native platinum or osmiridium, usually in association with gold, as small to minute nuggets.

(78) *Detection in Base-metal Ores, Mattes, Slimes, Rocks, etc.*—The material is subjected to crucible fusion as in the dry assay for gold and silver. If the ore is very low-grade, as is usually the case, a number of fusions must be made and the lead buttons scorified into one with a liberal addition of silver. The lead button is cupelled, the cleaned silver bead dissolved in nitric acid, and the solution decanted from gold (if present) into a small beaker. The gold is washed free from silver, and dissolved in a few drops of dilute *aqua regia* in a small porcelain dish; any black insoluble particles (*a*) are collected and reserved.

The silver nitrate solution, if yellow, contains palladium; platinum imparts a darker tint to the solution. The liquid is evaporated to dryness, the silver nitrate fused (6) and dissolved in hot water, and the solution filtered. If a dark brown to black residue remains, it is washed free from silver, returned to the beaker, treated with a little *aqua regia* (1 : 1), and the acid evaporated. The residue is evaporated twice with a few drops of hydrochloric acid, dissolved in a minimum of water, and filtered if necessary through a minute pad of filter-pulp, which is repeatedly washed with a few drops of water (*b*). The filtrate (which may be yellow to orange) is evaporated with a very little ammonium chloride almost to dryness: a yellow crystalline precipitate consisting of octahedra when viewed through a microscope proves platinum to be present (84, $\beta$).

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[1] F. C. Robinson. *Trans. Inst. Min. Met.*, 1926, **35**, 423.

The filtrate from the chloroplatinate precipitate, if brownish-yellow, contains palladium, which is identified by the sensitive dimethylglyoxime test (85, $\beta$). The filtrate from the palladium precipitate, upon evaporation to dryness, leaves a residue of ammonium chloride, etc., which may show the pink colour characteristic of rhodium. More usually, however, the rhodium remains in the insoluble (*b*, *below*).

If soluble rhodium is present, the ammonium-chloroplatinate crystals obtained by evaporation as *above* may have a more or less pronounced green tinge; they may even be emerald-green.[1] Such a green tinge is an indubitable proof of the presence of rhodium with the platinum.

The small pulp filter (*b*) is extracted with dilute ammonia, and if a dark residue remains, it is ignited and added to residue (*a*). The combined insoluble fraction may contain rhodium, iridium, and ruthenium (osmium is lost during cupellation). The separate detection of the four rarer platinum metals is conducted along quantitative lines, the operations being described under § VII, (89).

It has been repeatedly proposed to apply examination of the surface of silver (and gold) beads, obtained by cupellation, with a low-power microscope as a means for the detection and even for the differentiation of the platinum metals.[2] It must be pointed out that this practice is risky and uncertain. Although 1 or 2 per cent. of platinum or palladium imparts a characteristic frosted appearance to the silver bead, whilst a high percentage of platinum results in semi-fused beads of cauliflower-like appearance, it is impossible to say definitely (without a great deal of specialized experience) in the case of minute amounts which metals are present, or even whether the bead contains any platinum metal at all. This is due to the fact that the appearance of the surface depends also on the cupelling temperature and on the rate of cooling of the bead, and that the platinum metals all interfere with one another's effects.[3] In all cases, chemical tests are essential for a reliable detection. Fortunately, the above procedure, based upon fusion of the nitrate obtained by solution of the silver bead, presents no serious difficulties.

(79) *Detection in Alluvial Material.*[4]—If coarse, the alluvial is screened through sieves of suitable aperture to eliminate coarse material. The undersize is reduced to uniform fineness by crushing and screening (*e.g.* 60-mesh), the sieves used being ultimately examined for coarse yellow or white to grey nuggets.

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[1] Deville and Stas's "vert de platine."

[2] *E.g.* C. O. Bannister and G. Patchin, *Trans. Inst. Min. Met.*, 1914, **23**, 163.

[3] E. C. Forbes and F. E. Beamish, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 397.

[4] *Cf.* R. A. Cooper, *J. Chem. Met. Min. Soc. S. Africa*, 1922, **22**, 152.

The crushed (or the original fine, sandy) material (500 g.) is concentrated by panning, the tailings being caught in a large basin and retreated. The concentrate is gradually fed into hot nitric acid, which dissolves sulphides, arsenides, etc. The residue is collected, washed free from nitrates, and digested in a platinum or gold-plated silver dish with hydrochloric and hydrofluoric acids for the elimination of silicates.

At the operator's discretion, the insoluble residue from the preceding operation is fused with sodium bisulphate and the melt taken up with dilute acid, for the partial or complete elimination of certain minerals such as ilmenite, chromite, and zircon.

The final residue from the above extractions may still require concentration. This is best done on a small unpolished wooden *batea* or by careful washing from one beaker into another by means of a fine jet of water from a wash-bottle, and retreatment of the tailings until no further concentrate of metallic appearance is obtained. The total concentrate is dried, weighed, and attacked with *aqua regia*. The resultant solution is decanted or filtered and evaporated to dryness, the residue evaporated twice with hydrochloric acid, and the acid chloride solution evaporated with a moderate excess of ammonium chloride until the salt begins to crystallize. This may produce a yellow crystalline precipitate (platinum), a greenish-yellow to green precipitate characteristic of a subordinate amount of rhodium in association with platinum (78), or a reddish-yellow to brick-red precipitate indicating iridium in association with platinum. The filtrate is tested with ferrous chloride for gold, and with dimethylglyoxime for palladium.

The residue from the *aqua-regia* attack is washed, dried, and examined under a low-power microscope, if necessary, for metallic particles (osmiridium). This is identified by fusion with a little sodium peroxide (18) and distillation in a current of chlorine (43). The brownish-red colour of the ruthenium distillate is a most sensitive test for that element; by evaporation of the acid chloride solution almost to dryness, a quantity well below 0·0001 g. is readily detected. The distillation test for osmium is less sensitive, but a positive ruthenium reaction renders the presence of its associates, osmium and iridium, more than probable, or almost certain. The procedure for the detection of osmium and iridium is the same as that for their determination (§ VII, 89).

(80) *Specific Osmium Reactions.*—The outstanding property of osmium, shared by no other element, is the conversion of its soluble compounds into a volatile oxide ($OsO_4$) by the action of nitric acid. The same oxide is formed by simple ignition of the precipitated metal or (though much less readily) of native osmiridium. The vapour of osmium tetroxide has a pungent, unmistakable, and most unpleasant odour, recalling that of ozone at high concentrations. It is so penetrating that a fraction of a mg. of osmium can thereby be detected with certainty. Attention has been drawn to the harmful physiological effects of osmium tetroxide (§ II, *b*, 1, *a*); hence the smelling test should be performed with care on a minute amount (a few mg.) of material.

(*a*) Finely divided osmium (obtained by ignition of the sulphide or hydroxide in hydrogen) volatilizes upon ignition in air, emitting a penetrating ozone-like smell. Native osmiridium also evolves osmium tetroxide when strongly ignited. A colourless Bunsen flame becomes luminous in contact with the vapour of osmium tetroxide.

(β) For a chemical test, the material is fused with sodium peroxide, and the aqueous solution of the melt treated with excess of nitric acid and distilled into sodium hydroxide solution (42). The first fraction of the distillate diffusing into the alkaline solution produces a yellow to orange coloration. The yellow alkaline solution, when warmed and treated with alcohol, turns mauve; with small quantities of osmium, the solution is decolorized. When neutralized with sulphuric acid and boiled, it gives a black precipitate of osmium hydroxide, which may be collected, dried, and subjected to the smelling test (α, *above*).

(γ) Finely divided osmium (*cf.* α, *above*) dissolves slowly in strong, alkaline hypochlorite solution, giving an orange-yellow solution.

(81) *Specific Ruthenium Reactions.*—The characteristic ruthenium compound is the volatile, yellow tetroxide (*q.v.*, § II, *b*, 2, α), which is as important for the detection of the element as it is for its quantitative separation. The first step towards the identification of ruthenium in a solution containing other platinum metals and any other elements consists in distillation of the alkaline liquid (insoluble materials having been previously fused with sodium peroxide) in a current of chlorine (43) or with bromate (44). In these operations, osmium volatilizes with the ruthenium, but is carried over by the steam into the next receiver, while the ruthenium tetroxide undergoes reduction to the deep reddish-brown chloride in contact with the hydrochloric acid contained in the first receiver. The technique of the operation is fully described under (43). For qualitative work a single receiver containing hydrochloric acid (1 : 1) may be used. When the distillation is over, the contents of the receiver may be transferred to a beaker and evaporated to dryness in a fume-cupboard for the removal of any osmium tetroxide present. The residue consists of ruthenium trichloride.

(α) The production of a reddish-brown distillate under the conditions of the chlorine distillation is absolutely specific for ruthenium; further proof is unnecessary. The reaction is very sensitive (79).

(β) A dilute solution of ruthenium trichloride, when made ammoniacal and boiled after addition of a crystal of sodium thiosulphate, assumes an intense violet colour.

(γ) Finely divided metallic ruthenium dissolves in alkaline hypochlorite solution, to which it imparts a deep yellow to orange colour (*cf.* osmium, 80, γ).

(82) *Specific Rhodium Reactions.*—The reactions of rhodium are less pronounced than those of the other platinum metals, and the element is easily masked by the presence in the solution of preponderating amounts of iridium, platinum, or palladium. Rhodium is devoid of sensitive characteristic precipitation reactions, but is distinguished from the other platinum metals by the fine rose-red colour of its " double " chlorides. The colour of a solution of sodium chlororhodite is almost indistinguishable from that of a cobaltous chloride solution. The identification of rhodium hinges on its isolation as a more or less pure " double " chloride of characteristic colour.

(α) Pure, finely divided rhodium (*e.g.* precipitated by zinc), when intimately mixed with 2 parts of sodium chloride and strongly heated in a current of moist chlorine (22), furnishes a garnet-red melt soluble in water with a rose-red colour. The same result is obtained by solution of rhodium sulphide in *aqua regia* and evaporation of the solution with sodium chloride.

($\beta$) If the preceding test is applied to a mixed platinum-metals precipitate, the colour of the aqueous solution of the melt may be a pale or deep brownish-red to yellow. The liquid is evaporated to dryness on the water-bath with a drop of hydrochloric acid and very little sodium chlorate, the moist residue extracted with alcohol, the extract decanted off, and the residue again extracted with small portions of alcohol until this remains colourless. If rhodium is present, the final insoluble residue will be coloured pink to rose-red, sodium chlororhodite being insoluble in alcohol, whilst the chloroplatinate, chloropalladite, and chloriridate are soluble (sodium chloriridite is insoluble).

($\gamma$) An acid chloride solution containing several platinum metals, with or without gold, is treated with a little lead nitrate and evaporated until crystals of lead chloride separate. The mother-liquor is cooled, decanted off, and the crystals washed with small portions of water; they will be of a fine, delicate rose-pink colour if minute amounts of rhodium are present.[1]

($\delta$) The greenish-yellow to green colour of ammonium chloroplatinate gradually precipitated by evaporation of a mixed solution (78) indicates the presence of subordinate amounts of rhodium.

(83) *Specific Iridium Reactions.*—($\alpha$) A mixture of finely divided iridium and 2 parts of sodium chloride, when strongly heated in a current of moist chlorine, gives a dark brown mass, soluble in water to a deep brown solution. Slight sublimation of sodium chloriridate takes place during the heating, resulting in a faint deposit on the inside of the lid of the Rose crucible; the sublimate, moistened with a drop of water, gives a brown solution. The formation of this sublimate is a certain indication of iridium in admixture with other platinum metals. When iridium sulphide is dissolved in *aqua regia* and the solution evaporated with sodium chloride, a dark brown mass of sodium chloriridate is obtained, as in the fusion with sodium chloride in a current of chlorine.

($\beta$) The deep brown solution obtained as under ($\alpha$), when evaporated with a small excess of ammonium chloride, yields a lustrous, black, crystalline precipitate of ammonium chloriridate. The precipitate, when finely powdered, gives a red streak. If the cold chloriridate solution is treated with excess of solid ammonium chloride, the ammonium salt is precipitated as a more or less amorphous, dark red powder.

($\gamma$) A common solution of sodium chloriridate and chloroplatinate gives with ammonium chloride a mixed precipitate, the depth of colour of which increases with the relative proportion of iridium. With a fiftyfold excess of platinum over iridium, the colour of the precipitate is brick-red.

($\delta$) The brown solution of sodium chloriridate is bleached by addition of reducing agents such as stannous chloride, ferrous sulphate, oxalic acid, sodium nitrite, etc. When heated with a solution of caustic alkali, it gives a blue precipitate of iridium hydroxide.

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[1] W. R. Schoeller, *Analyst*, 1930, **55**, 553.

(84) *Specific Platinum Reactions.*—(α) Platinum is soluble in *aqua regia*; the solution, freed from nitric acid by evaporation, and re-evaporation with hydrochloric acid, gives a brown residue soluble in water to an orange solution.

(β) The solution obtained as under (α) gives with ammonium chloride a characteristic yellow crystalline precipitate (78). If an excess of ammonium chloride is added to the cold, fairly strong solution, the precipitate will be amorphous and pale yellow; if, on the other hand, a fairly dilute chloroplatinic acid solution is evaporated with a small excess of ammonium chloride, the precipitate deposits in the form of coarse, orange-yellow crystals.

(γ) When treated with stannous chloride, the yellow solution of chloroplatinic acid turns deep red (74).

(85) *Specific Palladium Reactions.*—(α) Palladium dissolves in *aqua regia*, the acid in contact with the metal assuming a vivid red colour due to the formation of chloropalladic acid. On evaporation of the solution to dryness and re-evaporation with hydrochloric acid, brown chloropalladous acid remains.

(β) The dilute, acid solution of chloropalladous acid gives with dimethylglyoxime solution a voluminous orange-yellow precipitate. At high dilutions the precipitate appears yellow. The reaction is absolutely specific, highly sensitive, and unaffected by the presence of other platinum metals (for coprecipitation of platinum, see 46, α).

(γ) Potassium iodide produces in palladium solutions a characteristic, black, flocculent precipitate soluble in excess, the solution turning red.

**§ VII. Determination in Ores and Low-grade Raw Materials.**—For the sake of convenience and in order to avoid repetition, this subsection will deal only with the determination of the platinum metals in low-grade materials such as base-metal ores, mattes, speisses, slimes, etc. The analysis of high-grade concentrates such as native platinum and osmiridium, on the other hand, will be described under § VIII on "Complete Analysis," because these enriched products consist chiefly of platinum metals, the determination of which is almost tantamount to a complete analysis.

(86) *Determination in Base-metal Ores, Speisses, Sweeps, Rocks, etc.*—In all cases the separation and determination of the platinum metals is preceded by fusion of the ore with litharge, flour, and fluxes, as in the fire assay for gold and silver, which yields a lead button containing the noble metals. In the great majority of cases, several portions of the ore must be smelted and the lead buttons scorified into one so that weighable amounts of precious metals may be obtained. If the ore contains refractory minerals such as chromite and zircon, it should be very finely crushed (below 150-mesh).[1] Iron nails should not be used in the reduction, because iridium and ruthenium have a greater affinity for iron than for lead. If an excess of silver is required in the charge (see 87), it is advantageous to add it in the form of precipitated dry silver chloride,[1] as the powder can be thoroughly mixed with the charge, while its mode of preparation from chemically pure silver nitrate is a guarantee that no trace of other precious metals finds its way into the charge.

Two methods are available for the determination, the one proceeding from the lead button obtained by crucible fusion (or scorification), the other from the silver bead left after cupellation of the lead button. The latter method is applied to the assay for platinum and palladium, the two commoner platinum metals, with only traces of the other members of the group (osmium is lost in the cupellation—see 4). The lead-button method, which is more elaborate, must be used for the determination of osmium, appreciable quantities of iridium, ruthenium, and rhodium, with or without platinum and palladium, and for any materials suspected to contain osmiridium (see 89). The silver bead may be treated with either sulphuric acid (87) or nitric acid (88).

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[1] C. W. Davis, *Tech. Paper* 270, *U.S. Bureau of Mines*, 1921, p. 13.

(87) *Silver Bead: Sulphuric-acid Parting.*—In this and the following process (88) an excess of silver in the charge is required. It lessens the risk of cupellation loss, particularly volatilization loss of palladium, and ensures the thorough removal of lead by cupellation and solution of the silver in the parting operation. Addition of silver chloride to the charge is desirable (86), but silver nitrate and metallic silver are also used. The amount of silver present should be from 30 to 50 times that of the combined platinum metals *plus* gold.

Sulphuric-acid parting is confined to ores containing only gold, platinum, and palladium as payable constituents in quantities of less than 5 oz. per ton. For richer materials nitric-acid attack should be applied (88).

When the silver bead has been dissolved in sulphuric acid and the latter diluted with water as under (7), the filtered solution contains, besides silver, nearly all of the palladium. The silver is precipitated with dilute hydrochloric acid, the chloride precipitate allowed to settle in the dark, the clear liquid filtered, and the precipitate retreated as under (25, $\beta$) unless white, *i.e.* free from palladium. The palladium is recovered from the filtrate or combined filtrate by precipitation with zinc (15), and is added to the residue from the sulphuric-acid parting; the combined precipitates are dissolved in *aqua regia*. The acid is evaporated, the residue taken up in dilute *aqua regia*, and the palladium precipitated with dimethylglyoxime (46, $\alpha$). The filtrate, freed from excess of precipitant by evaporation to dryness and digestion with a little sodium chlorate, contains gold and platinum. The former is precipitated with hydrazine (29), and the latter with the same reagent after evaporation of the acid and neutralization with sodium carbonate (63).

(88) *Silver Bead: Solution in Nitric Acid.*—This method is applicable to materials high or low in platinum and palladium, free from or containing only very subordinate amounts of rhodium, ruthenium, and iridium; osmium is not recovered (4).

Excess of silver is necessary for satisfactory cupellation as in the preceding method (87). The silver bead is dissolved in nitric acid (1 : 1), and the solution evaporated to dryness; if the amount of residual silver nitrate appears too small for a satisfactory fusion, a suitable amount of strong C.P. silver nitrate solution should be added; an excess of this does no harm, in fact is an advantage. The solution is evaporated to dryness, and the silver nitrate fused, set aside till cold, and dissolved in hot water, etc. as described under (6). This sequence of operations results in an *aqua-regia* solution containing gold, platinum, and palladium (for separation, see 87) and a residue which may contain rhodium, ruthenium, and iridium. This is ignited, reduced, and weighed as a check; it is transferred to a small nickel crucible, fused with a little sodium peroxide (18), and the aqueous solution of the melt transferred to a 250-ml. distillation flask and distilled for ruthenium (20, 44, and 60). The residual solution is worked up as shown under (21), the precipitate produced by sodium hydroxide being dissolved in *aqua regia* and the solution (after removal of silica: 21) evaporated with a little ammonium chloride for the precipitation of iridium (49). The filtrate, containing the rhodium with nickel derived from the crucible, is precipitated with zinc (15), and the ignited small precipitate identified by fusion with sodium chloride in chlorine (22). The rhodium is then determined with hydrazine (71).

If significant amounts of iridium, rhodium, or ruthenium are present in the material, cupellation involves risk of loss through partial oxidation of the precious metals, some of the oxide adhering to the cupel. In such cases, the lead-button method (89) should be used.

(89) *Lead Button: Solution in Nitric Acid.*—The clean lead button is treated as directed under (2), yielding two soluble fractions and an insoluble residue. The former are worked up for platinum, palladium, and rhodium (silver, gold) by the methods described under (33) and (50); the latter, containing osmium, iridium, and ruthenium, is treated by fusion with sodium peroxide (18), distillation (43 or 44), and recovery of the iridium from the residual solution as hydroxide (21), which is converted into ammonium chloriridate (10). If osmium or osmiridium is known or suspected to be present in the material under treatment, it is always safest not to ignite the residue prior to sodium-peroxide fusion lest a fraction of the osmium be lost by volatilization as tetroxide. The residue (after *aqua-regia* extraction, 2) may be collected in a porcelain dish, left to settle, the liquid decanted through a filter, the residue dried in the dish, and brushed into a nickel crucible; the filter is ignited, and the ash added.

If the osmium content is sufficiently high (as with some slimes and speisses), the original material may be fused with sodium peroxide (in one or more 2·5-g. charges) and the solution of the melt distilled with nitric acid (42). In this case no precautions are necessary in the examination of the lead button, the osmium distillate being rejected.

(90) *Determination in Copper-Nickel Ores, Mattes, and Copper Bullion.*—In the assay of sulphide ores containing much copper and nickel (*e.g.* flotation concentrates), the base metals find their way into the lead button and give trouble in the cupellation (4, 8). The following combination process is recommended:

(*a*) *Ores.* The ore (25 g.) is boiled with strong hydrochloric acid, which dissolves the sulphides. The acid is diluted, filtered, and the residue (*A*) washed, dried, and reserved.

The filtrate is saturated with hydrogen sulphide, the precipitate collected, washed with 2 per cent. sulphuric acid containing hydrogen sulphide, dried, added to *A*, and the whole roasted at 600° C. The calcined mass is leached with 5 per cent. sulphuric acid, and the residue (*B*) is washed and dried.

The last filtrate should be tested for precious metals by addition of 1 g.

of zinc powder, which displaces copper from the solution. The latter is then boiled for 10 minutes, filtered, and the copper precipitate digested with cold 10 per cent. ferric sulphate solution in 5 per cent. sulphuric acid, added in small portions, until the copper has nearly dissolved. The small residue is collected, added to *B*, and the mixture submitted to crucible fusion (86 or 87).

(β) *Low-grade copper matte and copper-nickel matte.* Low-grade copper matte (*i.e.* iron-copper matte) and copper-nickel matte are ground to 100-mesh and treated as under (α), *i.e.* by extraction with hot strong hydrochloric acid (the extract is free from platinum metals), calcination of the residue followed by sulphuric-acid leaching (single or double treatment), treatment of the extract with zinc, and crucible fusion or scorification of the combined residues.

(γ) *High-grade copper matte* (*i.e.* substantially pure copper sulphide low in iron) is roasted and leached with sulphuric acid, etc. In other words, the treatment is the same as that under (α), except that no preliminary hydrochloric-acid extraction is necessary.

(δ) *Copper bullion.* Portions of 25 to 50 g. are dissolved in nitric acid, which is evaporated, and the dry residue gently calcined until the red fumes are expelled. The residual copper oxide is dissolved in hot 5 per cent. sulphuric acid, and the unfiltered solution boiled with 1 g. of zinc powder, etc. as under (α). The precipitate is cupelled with silver, etc. (4).

**§ VIII. Complete Analysis of Concentrates, Metals, and Alloys.**—The concentrates comprise native platinum (91), South African platinum concentrates (92), and osmiridium (93). Succinct directions are given for the examination of the commercial platinum metals (94 to 99) and of a few alloys (100 to 102).

(91) *Native Platinum.*—The ore is a concentrate obtained from alluvial deposits, and consists chiefly of native platinum (*q.v.*, § I, *a*, 1), with subordinate and varying quantities of osmiridium, gold, and non-metallic matter (chromite, ilmenite, garnet, etc.) termed " sand." The constituents of the platinum and gold grains are soluble in *aqua regia*; the osmiridium and sand are insoluble. The sand, which is the only worthless constituent of the ore, may be determined by fusion with silver, as described under (8), either before or after attack with *aqua regia.*

The sample must be carefully prepared by quartering down, and a quantity of 20 or 40 g. (according to the degree of coarseness) weighed into a 1000-ml. conical flask. The acid mixture is prepared from 3 parts of hydrochloric acid, 1 part of nitric acid, and 1 part of water by volume. The ore is boiled with 250-ml. portions of mixed acids until the action slackens, when the liquid is carefully decanted into a beaker and the residue in the flask attacked with fresh acid. While the attack proceeds, the decanted solution is filtered into a 1000- (or 2000-) ml. graduated flask. When the second portion of acid is spent, it is decanted and filtered in the same manner as the first, and a third smaller portion of fresh acid is added to the residue. The attack is complete when a fresh portion of acid remains colourless after boiling or acquires only a pale yellow (not orange) tinge. The black residue is collected on the filter, the flask being kept in an inclined position over the funnel to allow the finely divided osmiridium to run down with the stream of wash-liquor (1 to 2 per cent. hydrochloric acid, pure water usually giving a turbid black filtrate).

(α) *Osmiridium and sand.* The filter containing the insoluble residue is dried, the residue detached as completely as possible, the paper ignited, and the ash weighed together with the bulk of the insoluble. This is transferred to a scorifier, mixed with 50 to 100 g. of granulated pure lead, and the mixture covered with litharge and heated to bright redness in a muffle. When cold, the scorifier is broken, and the lead button carefully freed from slag by gentle tapping (not hammering) and digestion with cold dilute hydrofluoric acid if necessary. The button is dissolved in dilute nitric acid, and the osmiridium washed, dried, and weighed. It is usually reported as such in platinum-ore analysis, but may of course be analysed separately according to method (93).

(β) *Aqua regia solution.* This is made up to volume, and two or three 50-ml. portions are transferred to squat 250-ml. beakers by means of a standardized pipette. Each portion is evaporated to a syrup on the water-bath, moistened with a little hot water, and evaporated with 10 ml. of hydrochloric acid. A second evaporation with hydrochloric acid is necessary, after which the residue is dissolved in N. hydrochloric acid.

(γ) *Gold.* The hot acid solution, obtained as under (β), is cautiously treated with sulphurous acid. The precipitated gold is allowed to settle, collected, and washed with dilute hydrochloric acid. After ignition it should be yellow, not discoloured, otherwise it must be dissolved and reprecipitated.

(δ) *Platinum and iridium.* The filtrate or combined filtrate from the gold is evaporated, and the residue oxidized by addition of a little sodium chlorate solution followed by evaporation to pastiness. The residue is dissolved in hot N. hydrochloric acid, the solution precipitated with ammonium chloride (10), and the precipitate $P^1$ purified by the chlorine process (11). The precipitate $P^2$ is cautiously ignited in a tared Rose crucible (12). The combined filtrates from $P^1$ and $P^2$ are boiled with a little sodium chlorate and evaporated (10), yielding a small dark precipitate, $P^{1a}$, which is ignited and extracted as under (49), the insoluble fraction being added to $P^2$. The minor platinum fraction, $P^{2a}$, is precipitated in the extract from $P^{1a}$ (see 49) and also added to the Rose crucible, which now contains the total platinum and iridium. They are ignited, reduced, weighed, and separated by fusion with lead (3). The iridium is weighed, and the platinum found by difference.

(ε) *Palladium.* The combined filtrates from $P^{1a}$ and $P^{2a}$ are saturated with hydrogen sulphide, rendered ammoniacal, warmed, re-acidified with hydrochloric acid, and set aside at about 60° C. until the precipitate has settled. This is collected, preferably on a porous glass filter, and washed as usual; it contains all the copper, palladium, and rhodium, possibly traces of platinum, and most of the nickel. It is dissolved in *aqua regia*, which is evaporated until 1 to 2 ml. is left. After dilution with water, the palladium is precipitated with dimethylglyoxime (68).

(ζ) *Rhodium.* The filtrate from the palladium precipitate is evaporated to dryness, the residue being again evaporated with *aqua regia*, and once more with hydrochloric acid. The final residue is dissolved in acidulated water, and the solution treated by the nitrite process (16). The precipitate (copper and nickel) is filtered off and retreated, and the combined filtrate evaporated to dryness with hydrochloric acid. It contains the rhodium and a trace of platinum, if any, which are precipitated as under (71).

($\eta$) *Base metals.* These are determined in the precipitate obtained in the nitrite separation (copper and most of the nickel); and in the filtrate from the hydrogen-sulphide precipitate (iron and balance of the nickel).

(92) *South African Platinum Concentrates.*—These concentrates differ from all other platinum ores in that they contain platinum and palladium minerals insoluble in *aqua regia*, but soluble after roasting in air, which removes arsenic, antimony, and sulphur. The whole of the material can normally be crushed to 100-mesh size, hence portions of 1 g. can be taken for analysis.

($\alpha$) *Platinum and base metals.* The ore is extracted with hot strong hydrochloric acid, and the extract diluted and filtered. It contains iron, but is free from platinum metals.

The washed residue is strongly ignited in a porcelain crucible, cooled, and attacked with *aqua regia*. The acid is evaporated, and the nitric acid destroyed by double evaporation with hydrochloric acid. The residue is taken up with N. hydrochloric acid, and the solution filtered and analysed for platinum and associated metals as under (91, $\beta$ to $\eta$).

The residue insoluble in *aqua regia* is ignited and weighed. It consists of chromite with a little ruthenium, etc. derived from a small admixture of laurite in the concentrate. The insoluble metal may be determined in the combined residues from several assays by scorification with lead and litharge (91, $\alpha$).

($\beta$) *Sulphur and arsenic.* One g. of ore is fused with sodium peroxide in a nickel crucible. The melt is taken up with hot water, the suspension boiled with alcohol, and the precipitate filtered off. The filtrate is analysed for sulphate and arsenate in separate portions.

($\gamma$) *Antimony*, if present, is soluble in *aqua regia*. The solution of 1 to 2 g. of ore is evaporated, the platinum precipitated with ammonium chloride, and the antimony in the filtrate with hydrogen sulphide. The sulphide precipitate is extracted with potassium sulphide, and the antimony determined as usual in the filtrate.

(93) *Osmiridium.*[1]—This mineral is opened up by fusion with sodium peroxide (18), which must, however, be preceded by a fusion process with zinc for the purpose of converting the hard, crystallized native alloy into an amorphous mass, easily reduced to an impalpable powder by grinding.

The concentrate is carefully quartered down to 2 to 3 g., which is accurately weighed, and transferred to a cylindrical crucible of purified gas-carbon (as used for fusions with lead—see 3), together with 8 to 10 g. of chemically pure zinc. The crucible is covered, placed inside a small fireclay pot, which is then filled with charcoal of bean size, closed with a lid, and heated in a muffle at about 600° C. for half an hour to allow the osmiridium to dissolve in the molten zinc. The heat is then gradually raised above the boiling-point of zinc, the vapour of which escapes, forming dense fumes of zinc oxide. When the evolution of fumes ceases, the heat is raised to over 1000° C. for half an hour, after which the muffle is allowed to cool, and the clay pot withdrawn. When cold, the contents of the carbon crucible are accurately weighed, the porous metallic mass showing a slight increase in weight owing to retention of a little zinc. It is ground to a very fine powder in an agate mortar, and a quantity of material equivalent to 1 g. of the original mineral weighed into a nickel crucible.

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[1] After Leidié and Quennessen, *Compt. rend.*, 1903, **136**, 1399.

The sodium-peroxide fusion and lixiviation are carried out as under (18). The suspension is transferred to the distillation flask forming part of the train described under (20), digested overnight with electrolytic hypochlorite solution (43), and distilled in a current of chlorine or with bromate (43 or 44).

The distillation yields three products, *viz.* an osmium distillate (58); a ruthenium distillate (60); and the residual solution, which is worked up as under (43, β), giving an ammonium-chloride and a zinc precipitate. The combined ignited and reduced precipitates are fused with lead (3), and the resultant lead button is extracted with acids (2), giving a residue of pure iridium (or iridium containing the minor ruthenium fraction if chlorine distillation has been used) and two acid extracts containing platinum, rhodium, and usually gold; these latter are treated as under (2) and (33). Palladium does not normally occur in osmiridium, and the only base metals found in the mineral are iron and copper in minute quantities.

(94) *Refined Platinum.*—The platinum of commerce is now very pure (over 99·9 per cent.). It contains traces of other platinum metals, with iron and possibly copper. These are determined in two 20-g. portions.

(*a*) *Platinum metals.* The metal is dissolved in *aqua regia* and converted into sodium chloroplatinate (9). The solution is submitted to bromate hydrolysis (47), and the precipitate analysed for palladium, rhodium, and iridium.

(*β*) *Base metals.* The platinum is converted into chloroplatinic acid (9), the hot solution of which is cautiously and gradually precipitated with a calculated deficiency of ammonium chloride (10·7 g.). The filtrate is evaporated to dryness and treated by the nitrite method (16), the precipitate containing the iron and copper.

(95) *Palladium.*—Commercial palladium is of a high degree of purity, owing to the method of its preparation from purified dichlorodiammine-palladium. The only impurity usually encountered is a minute amount of platinum. This is determined in one or more 5-g. portions by solution in *aqua regia*, evaporation with hydrochloric acid (9), precipitation of the solution with a calculated deficiency of potassium iodide (46, β), filtration under slight suction, and precipitation of the balance of the palladium in the filtrate with dimethylglyoxime. The last filtrate is evaporated to dryness with *aqua regia*, the residue again evaporated with hydrochloric acid, and the acid chloride solution reduced with pure zinc (15). The combined precipitates (if more than one portion was taken) are ignited, dissolved in *aqua regia*, and the platinum precipitated with ammonium chloride (10).

(96) *Iridium.*—(*a*) In a 2-g. portion, osmium and ruthenium are detected

and determined by fusion with sodium peroxide (18) and distillation with bromate (44).

(β) Another 2-g. portion is ignited in a current of hydrogen in a tared porcelain crucible, the iridium *plus* crucible being weighed before and after reduction. The difference gives oxygen. The metal is brushed into a gold basin and heated with hydrofluoric and sulphuric acids until fumes are evolved. The residual metal is collected, washed with water, hot ammonium acetate solution, and again with water, ignited under hydrogen in a tared porcelain crucible, and weighed. The loss gives silica, provided the extracts, when tested with ammonium sulphide, give no darkening due to base metals.

The recovered metal is next fused with lead in a carbon crucible (3), and the lead button extracted with acids (2), the extracts being tested for rhodium and platinum.

(γ) A separate iron determination is made by fusion of 1 to 2 g. of iridium with potassium hydroxide and nitrate in a gold crucible (19). The mass is taken up with water, the suspension boiled with alcohol, the precipitated hydroxide collected, and dissolved in *aqua regia* (21). The solution is cautiously precipitated with ammonium chloride, yielding $P^1$ and $P^{1a}$ (10); the filtrate from the latter is precipitated with ammonia, and the precipitate collected, dissolved in hydrochloric acid, and freed from traces of platinum metals by the nitrite process (16). The precipitate thus obtained is dissolved in hydrochloric acid, reprecipitated with ammonia, and ignited to ferric oxide.

(97) *Rhodium.*—(*a*) *Platinum metals.* The metal is fused with lead in a carbon crucible (3), the button dissolved in 15 per cent. nitric acid, and the filtered extract precipitated with 40 to 50 ml. of sulphuric acid (1 : 1). The lead sulphate is filtered under suction, and the filtrate returned to the original beaker, together with the filter containing the insoluble from the nitric-acid treatment, and 5 g. of ammonium sulphate. When the paper has been destroyed, the beaker is covered and the sulphuric acid vigorously boiled for 10 to 15 minutes, the rhodium dissolving. When cold, the acid is diluted with 100 ml. of water, and the beaker is set aside in an inclined position for some hours. The clear liquid is poured off, and the deposit boiled as before with 15 ml. of sulphuric acid and a little ammonium sulphate. The cold acid is diluted, set aside overnight, and filtered, together with the first extract.

The insoluble residue is freed from lead sulphate by ammonium acetate solution, and then extracted with 15 per cent. *aqua regia* (2). The residue, unless small and obviously crystalline, should again be fused with 5 g. of lead, and the above operations repeated. The products are: a combined sulphate extract; a combined *aqua-regia* extract; and the insoluble residue, which is analysed for iridium, ruthenium, and osmium (18). The extracts are worked up as explained under (33) for the recovery of platinum, palladium, and possibly gold. Rhodium is not determined, but is taken by difference.

(β) *Iron.* One g. or more of rhodium is fused with 5 to 10 g. of pure granulated zinc in a covered porcelain crucible, ammonium chloride being sprinkled on to the molten metal to maintain a bright clean surface free from oxide crusts. The cooled zinc button is washed, dissolved in hydrochloric acid, and the spongy rhodium filtered off. The filtrate is treated with excess of ammonia, and the precipitate collected, dissolved, reprecipitated, and ignited to ferric oxide. This may have to be purified by the nitrite process (16).

(98) *Osmium.*—(α) The analysis is preceded by ignition in air, which volatilizes the bulk of the osmium as tetroxide. The operation must be conducted in an efficient draught-chamber. The elimination of the osmium is facilitated at the concluding stage of the ignition by trituration of the cooled residue with a glass rod, reduction with coal-gas (13), and re-ignition. The residue is weighed, and tested for silica with hydrofluoric acid, and for iron, etc. by fusion with bisulphate.

(β) Osmium, ruthenium, and iridium are determined by fusion with sodium peroxide, distillation, and examination of the residual solution (18, 43 or 44, and 43, β).

(99) *Ruthenium.*—(α) Ignition loss and silica are determined as under (96, β).

(β) Ruthenium, osmium, and other platinum metals are determined by fusion with sodium peroxide (18) and bromate distillation (44); the small amount of osmium, if any, is determined as sulphide (59). The major ruthenium fraction is precipitated with ammonium chloride (61). The residual liquor from the distillation is worked up for iridium, platinum, and rhodium (21).

(100) *Contact Points and Platinum Crucibles.*—These consist of alloys of platinum and iridium. Contact points for magnetos contain up to 25 per cent. of iridium; crucibles of hardened platinum, about 3 per cent. The metal (1 g.) is fused with lead in a carbon crucible (3), the button dissolved (2), and the insoluble iridium residue ignited, reduced, and weighed. It should be tested for ruthenium and iron by fusion with potassium hydroxide and nitrate (19), distillation (44), and examination of the residual solution (21); and since this involves precipitation of the iridium as ammonium chloriridate (10), a direct iridium determination should be carried out (65).

(101) *Dental Alloys.*—A brief reference may be made to the analysis of dental gold alloys, which has been very fully investigated by W. H. Swanger[1] and R. Gilchrist.[2] These alloys are very complex, as the constituent metals include gold, silver, platinum, palladium, iridium, rhodium, tin, iron, zinc, nickel, magnesium, and indium. For a description of the lengthy procedures involved, the original papers must be consulted.

(102) *Jewellers' Platinum Alloys.*—The analysis of these alloys has been described by H. Holzer and E. Zaussinger.[3]

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[1] *Sci. Paper* **532**, *U.S. Bureau of Standards*, 1926.

[2] *Bureau of Standards J. Research*, 1938, **20**, 745; Abstract: *Analyst*, 1938, **63**, 848.

[3] *Zeitsch. anal. Chem.*, 1938, **111**, 321; Abstract: *Analyst*, 1938, **63**, 215.

## INTERNATIONAL ATOMIC WEIGHTS, 1940.

| | |
|---|---|
| Aluminium | 26·97 |
| Antimony | 121·76 |
| Argon | 39·944 |
| Arsenic | 74·91 |
| Barium | 137·36 |
| Beryllium | 9·02 |
| Bismuth | 209·00 |
| Boron | 10·82 |
| Bromine | 79·916 |
| Cadmium | 112·41 |
| Cæsium | 132·91 |
| Calcium | 40·08 |
| Carbon | 12·010 |
| Cerium | 140·13 |
| Chlorine | 35·457 |
| Chromium | 52·01 |
| Cobalt | 58·94 |
| Copper | 63·57 |
| Dysprosium | 162·46 |
| Erbium | 167·2 |
| Europium | 152·0 |
| Fluorine | 19·00 |
| Gadolinium | 156·9 |
| Gallium | 69·72 |
| Germanium | 72·60 |
| Gold | 197·2 |
| Hafnium | 178·6 |
| Helium | 4·003 |
| Holmium | 163·5 |
| Hydrogen | 1·0080 |
| Indium | 114·76 |
| Iodine | 126·92 |
| Iridium | 193·1 |
| Iron | 55·85 |
| Krypton | 83·7 |
| Lanthanum | 138·92 |
| Lead | 207·21 |
| Lithium | 6·940 |
| Lutecium | 174·99 |
| Magnesium | 24·32 |
| Manganese | 54·93 |
| Mercury | 200·61 |
| Molybdenum | 95·95 |
| Neodymium | 144·27 |
| Neon | 20·183 |
| Nickel | 58·69 |
| Niobium | 92·91 |
| Nitrogen | 14·008 |
| Osmium | 190·2 |
| Oxygen | 16·0000 |
| Palladium | 106·7 |
| Phosphorus | 30·98 |
| Platinum | 195·23 |
| Potassium | 39·096 |
| Praseodymium | 140·92 |
| Protactinium | 231 |
| Radium | 226·05 |
| Radon | 222 |
| Rhenium | 186·31 |
| Rhodium | 102·91 |
| Rubidium | 85·48 |
| Ruthenium | 101·7 |
| Samarium | 150·43 |
| Scandium | 45·10 |
| Selenium | 78·96 |
| Silicon | 28·06 |
| Silver | 107·880 |
| Sodium | 22·997 |
| Strontium | 87·63 |
| Sulphur | 32·06 |
| Tantalum | 180·88 |
| Tellurium | 127·61 |
| Terbium | 159·2 |
| Thallium | 204·39 |
| Thorium | 232·12 |
| Thulium | 169·4 |
| Tin | 118·70 |
| Titanium | 47·90 |
| Tungsten | 183·92 |
| Uranium | 238·07 |
| Vanadium | 50·95 |
| Xenon | 131·3 |
| Ytterbium | 173·04 |
| Yttrium | 88·92 |
| Zinc | 65·38 |
| Zirconium | 91·22 |

## GRAVIMETRIC FACTORS.

| Element. | Atomic Weight, 1940. | Known. | Required. | Factor. | Logarithm (Mantissa). |
|---|---|---|---|---|---|
| Beryllium | 9·02 | BeO | Be | 0·3605 | ·55692 |
| Cæsium | 132·91 | $Cs_2O$ | Cs | 0·9432 | ·97462 |
| | | CsCl | $Cs_2O$ | 0·8369 | ·92268 |
| | | $Cs_2SO_4$ | $Cs_2O$ | 0·7788 | ·89141 |
| | | $Cs_2PtCl_6$ | $Cs_2O$ | 0·4183 | ·62144 |
| | | $Cs_2PtCl_6$ | CsCl | 0·4998 | ·69876 |
| Cerium | 140·13 | $CeO_2$ | Ce | 0·8141 | ·91067 |
| | | $CeO_2$ | $Ce_2O_3$ | 0·9535 | ·97933 |
| Gallium | 69·72 | $Ga_2O_3$ | Ga | 0·7439 | ·87153 |
| | | $(C_9H_6ON)_3Ga$ | Ga | 0·1388 | ·14252 |
| Germanium | 72·60 | $GeO_2$ | Ge | 0·6941 | ·84141 |
| | | $GeS_2$ | Ge | 0·5310 | ·72511 |
| | | $Mg_2GeO_4$ | Ge | 0·3919 | ·59320 |
| | | $(C_{19}H_{22}ON_2)_4H_4.GeMo_{12}O_{40}$ | Ge | 0·02384 | ·37727 |
| Hafnium | 178·6 | $HfO_2$ | Hf | 0·8481 | ·92842 |
| Indium | 114·76 | $In_2O_3$ | In | 0·8271 | ·91753 |
| | | $(C_9H_6ON)_3In$ | In | 0·2097 | ·32164 |
| Lithium | 6·94 | $Li_2O$ | Li | 0·4645 | ·66701 |
| | | LiCl | $Li_2O$ | 0·3524 | ·54698 |
| | | $Li_2SO_4$ | $Li_2O$ | 0·2718 | ·43422 |
| | | $BaSO_4$ | $Li_2O$ | 0·1280 | ·10724 |
| Molybdenum | 95·95 | Mo | $MoO_3$ | 1·5003 | ·17617 |
| | | Mo | $MoS_2$ | 1·6683 | ·22227 |
| | | $MoO_3$ | Mo | 0·6666 | ·82383 |
| | | $MoO_3$ | $MoS_2$ | 1·1120 | ·04610 |
| | | $MoS_2$ | Mo | 0·5994 | ·77773 |
| | | $PbMoO_4$ | Mo | 0·2613 | ·41718 |
| | | $PbMoO_4$ | $MoO_3$ | 0·3921 | ·59335 |
| | | $PbMoO_4$ | $MoS_2$ | 0·4360 | ·63945 |
| | | $MoO_2(C_9H_6ON)_2$ | Mo | 0·2305 | ·36269 |
| Niobium | 92·91 | $Nb_2O_5$ | Nb | 0·6990 | ·84450 |
| Palladium | 106·7 | Pd | KI | 3·112 | ·49302 |
| | | $(C_4H_7N_2O_2)_2Pd$ | Pd | 0·3167 | ·50063 |
| Rhenium | 186·31 | $C_{20}H_{16}N_4HReO_4$ | Re | 0·3306 | ·51920 |
| | | $(C_6H_5)_4AsReO_4$ | Re | 0·2940 | ·46840 |
| Rubidium | 85·48 | $Rb_2O$ | Rb | 0·9144 | ·96114 |
| | | RbCl | $Rb_2O$ | 0·7729 | ·88815 |
| | | $Rb_2SO_4$ | $Rb_2O$ | 0·7002 | ·84521 |
| | | $Rb_2PtCl_6$ | $Rb_2O$ | 0·3229 | ·50912 |
| | | $Rb_2PtCl_6$ | RbCl | 0·4178 | ·62095 |
| Scandium | 45·10 | $Sc_2O_3$ | Sc | 0·6527 | ·81470 |

## GRAVIMETRIC FACTORS—*continued.*

| Element. | Atomic Weight, 1940. | Known. | Required. | Factor. | Logarithm (Mantissa). |
|---|---|---|---|---|---|
| Selenium . | 78·96 | Se | $SeO_2$ | 1·4053 | ·14776 |
| | | $SeO_2$ | $SeO_3$ | 1·1441 | ·05850 |
| Tantalum . | 180·88 | $Ta_2O_5$ | Ta | 0·8189 | ·91323 |
| Tellurium . | 127·61 | Te | $TeO_2$ | 1·2508 | ·09718 |
| | | $TeO_2$ | Te | 0·7995 | ·90282 |
| | | $TeO_2$ | $TeO_3$ | 1·1002 | ·04149 |
| Thallium . | 204·39 | $Tl_2CrO_4$ | Tl | 0·7789 | ·89150 |
| | | $Tl_2CrO_4$ | $Tl_2O$ | 0·8094 | ·90817 |
| | | Tl | $Tl_2O$ | 1·0391 | ·01667 |
| | | $Tl_2O$ | $Tl_2O_3$ | 1·0753 | ·03155 |
| | | TlI | Tl | 0·6169 | ·79023 |
| | | $NaTl_2Co(NO_2)_6$ | Tl | 0·5331 | ·72683 |
| | | $C_{10}H_7.NH.CO.CH_2.STl$ | Tl | 0·4860 | ·68653 |
| Thorium . | 232·12 | $ThO_2$ | Th | 0·8789 | ·94391 |
| | | $Th(SO_4)_2$ | $ThO_2$ | 0·6226 | ·79419 |
| Titanium . | 47·90 | $TiO_2$ | Ti | 0·5995 | ·77779 |
| Tungsten . | 183·92 | $WO_3$ | W | 0·7930 | ·89929 |
| | | W | $WO_3$ | 1·2610 | ·10071 |
| Uranium . | 238·07 | $U_3O_8$ | U | 0·8480 | ·92841 |
| | | $U_3O_8$ | $UO_2$ | 0·9620 | ·98318 |
| | | $U_3O_8$ | $UO_3$ | 1·0190 | ·00817 |
| | | $(UO_2)_2P_2O_7$ | U | 0·6668 | ·82397 |
| | | $(UO_2)_2P_2O_7$ | $UO_2$ | 0·7564 | ·87875 |
| | | $(UO_2)_2P_2O_7$ | $UO_3$ | 0·8012 | ·90374 |
| | | $(UO_2)_2P_2O_7$ | $U_3O_8$ | 0·7863 | ·89557 |
| Vanadium . | 50·95 | $V_2O_5$ | V | 0·5602 | ·74834 |
| | | $V_2O_5$ | $V_2O_3$ | 0·8241 | ·91597 |
| | | $NH_4VO_3$ | $V_2O_5$ | 0·7774 | ·89065 |
| Zirconium . | 91·22 | $ZrO_2$ | Zr | 0·7402 | ·86937 |
| | | $ZrP_2O_7$ | Zr | 0·4632 | ·66577 |

# MINERALOGICAL INDEX.

ACHREMATITE, 190.
Aeschynite, 146.
Allanite, 74.
Altaite, 167.
Amblygonite, 36.
Anatase, 86.
Ardennite, 129.
Argyrodite, 123.
Autunite, 221.

BADDELEYITE, 103.
Bastnäsite, 74.
Beckelite, 74.
Belonosite, 190.
Bertrandite, 46.
Beryl, 46.
Beryllonite, 46.
Berzelianite, 167.
Betafite, 146.
Bismuthotantalite, 145.
Blomstrandine, 146.
Brackebuschite, 129.
Braggite, 241.
Bravoite, 129.
Brazilian zirconia rock, 103.
Brazilite, 103.
Bröggerite, 220.
Brookite, 87.

CALAVERITE, 167.
Calciothorite, 117.
Caldasite, 103.
Canfieldite, 123.
Carnotite, 129.
Cerite, 74.
Chalcomenite, 167.
Chillagite, 207.
Chrysoberyl, 46.
Clausthalite, 167.
Cleveite, 220.
Coloradoite, 167.
Columbite, 145.
Cooperite, 241.
Copper uranite, 221.
Cordylite, 74.
Crookesite, 69.
Cuproscheelite, 207.
Cylindrite, 65.

DANALITE, 46.
Delorenzite, 75.
Descloizite, 129.

EUCLASE, 46.
Eucrasite, 117.
Eudialyte, 104.
Euxenite, 146.

FERBERITE, 207.
Ferganite, 129.
Fergusonite, 145.
Ferrocolumbite, 145.
Ferrotantalite, 145.
Frenzelite, 167.
Freyalite, 117.

GADOLINITE, 74.
Germanite, 60, 123.
Graphic tellurium, 167.
Guanajuatite, 167.
Guarinite, 87.

HAINITE, 103.
Hambergite, 46.
Hellandite, 74.
Helvite, 46.
Herderite, 46.
Hessite, 167.
Hübnerite, 207.
Hutchisonite, 69.

ILMENITE, 87.
Ilmenorutile, 146.
Ilsemannite, 190.
Iridosmine.—*See* "Osmiridium."
Iserine, 87.

KEILHAUITE, 75.

LANTHANITE, 74.
Laurite, 241.
Lavenite, 103.
Lepidolite, 36, 41.
Leucophanite, 46.
Liebigite, 221.
Lime uranite, 221.
Lithiophylite, 36.
Lorandite, 69.

MACKINTOSHITE, 117.
Manganocolumbite, 145.
Manganotantalite, 145.
Meliphanite, 46.
Menaccanite, 87.
Microlite, 145.
Molybdenite, 189.
Molybdic ochre, 189.
Molybdite, 189.

Monazite, 117.
Montebrasite, 36.
Mottramite, 129.

NAEGITE, 103.
Nagyagite, 167.
Naumannite, 167.
Nevjanskite, 241.

OCTAHEDRITE, 86.
Orangite, 117.
Orthite, 74.
Osmiridium, 241.

PALLADIUM, 241.
Parisite, 74.
Pateraite, 190.
Patronite, 129.
Perovskite, 87.
Petalite, 36.
Petzite, 167.
Phenacite, 46.
Phosphuranylite, 221.
Pilbarite, 117.
Pitchblende, 221.
Platiniridium, 241.
Platinum, 240.
Pollucite, 41.
Polycrase, 146.
Polylithionite, 36.
Powellite, 190.
Priorite, 146.
Pseudobrookite, 87.
Pucherite, 129.
Pyrophanite, 87.

RASPITE, 207.
Reinite, 207.
Rhodizite, 41.
Roscoelite, 129.
Rosenbuschite, 104.
Rowlandite, 74.
Rutherfordine, 221.
Rutile, 86.

SAMARSKITE, 145.
Scheelite, 207.
Selen-tellurium, 167.
Siserskite, 241.
Sperrylite, 241.
Sphene, 87.
Spodumene, 36.
Stibiopalladinite, 241.
Stibiotantalite, 145.
Stolzite, 207.
Strüverite, 146.
Sulvanite, 129.
Sylvanite, 167.

TAENIOLITE, 36.
Tantalite, 145.
Tantalocassiterite, 146.
Tellurite, 167.
Tellurium, 167.
Tetradymite, 167.
Thalenite, 75.
Thorianite, 117.
Thorite, 117.
Thorogummite, 221.
Thortveitite, 57.
Tiemannite, 167.
Titanite, 87.
Torbernite, 221.
Trimenite, 46.
Triphylite, 36.
Trögerite, 221.
Tungstenite, 207.
Tungstic ochre, 207.
Turanite, 129.

UHLIGITE, 103.
Ultrabasite, 123.
Uranic ochre, 221.
Uraninite, 220.
Uranites, 221.
Uranocircite, 221.
Uranoniobite, 221.
Uranophane, 221.
Uranosphaerite, 221.
Uranospinite, 221.
Uranothallite, 221.

VANADINITE, 129.
Volborthite, 129.
Vorobyevite, 41.
Vrbaite, 69.

WALPURGITE, 221.
Wiikite, 57.
Wolframite, 207.
Wulfenite, 189.

XENOTIME, 75, 118.

YTTRIALITE, 74.
Yttrocerite, 75.
Yttrocrasite, 75.
Yttrofluorite, 75.
Yttrogummite, 221.
Yttrotantalite, 145.
Yttrotitanite, 75.

ZEUNERITE, 221.
Zinnwaldite, 36.
Zippeite, 221.
Zircon, 103.
Zirkelite, 103.

# ANALYTICAL INDEX.

(In order to avoid duplication, and thus reduce the size of this Index, no entries have been made for the commoner elements. When searching for the separation of a commoner from a rarer element, the reader should consult the Index under the heading of the rarer element.)

ACID-EARTH group, Qualitative analysis of, 15.
Alkali group, Qualitative analysis of, 18.
Amblygonite, Complete analysis of, 41.
Ammonium chloride, Precipitation of platinum metals with, 254.
— — as reagent for platinum metals, 248.
Argon and other gases in uranium ores, 236.

BADDELEYITE, Complete analysis of, 115.
Beryl, Complete analysis of, 57.
Beryllium, Colorimetric determination of, 54.
—, Compounds of, 46.
—, Detection of, in minerals, 55.
—, Determination of, in minerals and rocks, 55.
—, Gravimetric determination of, 52.
—, Separation of, from aluminium, 47.
—, — —, — — and iron, 50.
—, — —, — chromium, 51.
—, — —, — iron, 50.
—, — —, — metals of the hydrogen-sulphide group, 47.
—, — —, — phosphoric acid, 52.
—, — —, — thorium, 52.
—, — —, — titanium, 51.
—, — —, — uranium, 52.
—, — —, — vanadium, 52.
—, — —, — zirconium, 52.
Bisulphate fusions, 3.
Brazilian zirconia rock, Complete analysis of, 115.

CÆSIUM, Compounds of, 42.
—, Detection of, in minerals, 45.
—, Determination of, in minerals and rocks, 45.
—, — —, — pollucite, 45.
—, Gravimetric determination of, 43, 44.
—, Separation of, from other alkali metals, 43.
—, — —, — rubidium and potassium, 42, 43.
Carnotite, Complete analysis of, 237.
Ceria, 76.
Cerium.—*See also* "Rare-earth metals."
—, Detection of, in minerals, 83.
—, Gravimetric determination of, 81.
Cerium, Separation of, from other rare earths, 79.
—, Volumetric determination of, 82.
— group, 75.
— —, Detection of, 83.
— —, Separation of, from yttrium group, 78.
Columbite, Complete analysis of, 166.
Columbium.—*See* "Niobium."
Complete chemical analysis, 18–36.
Contact points, Analysis of, 296.
Contamination by fusion, 2.
— in crushing, 2.
Crushing, Contamination in, 2.
— samples, 1.
Cupferron as a reagent for:
  Beryllium, Separation of, from titanium, 51.
  —, — —, — zirconium, 52.
  Gallium, Separation of, from aluminium, chromium, indium, uranium, and rare earths, 61.
  Niobium, Gravimetric determination of, 160.
  —, Separation of, from aluminium, chromium, and manganese, 150.
  Tantalum, Gravimetric determination of, 160.
  —, Separation of, from aluminium, chromium, and manganese, 150.
  Titanium, Determination of, in ilmenite, etc., 98.
  —, Gravimetric determination of, 94.
  —, Separation of, from aluminium, chromium, uranium, bivalent metals, and phosphoric acid, 92.
  Uranium, Separation of, from aluminium, chromium, and bivalent metals, 224.
  —, — —, — iron, vanadium, titanium, and zirconium, 224.
  —, — —, — zirconium, 227.
  —, — — uranic from uranous, 225.
  Vanadium, Gravimetric determination of, 135.
  —, Separation of, from aluminium, chromium, uranium, and bivalent metals, 131.
  —, — —, — phosphate, 132.

Cupferron as a reagent for:
  Vanadium, Separation of, from tungstate, 133.
  Zirconium, Determination of, in zircon, baddeleyite, etc., 112.
  —, Gravimetric determination of, 111.
  —, Separation of, from aluminium, chromium, uranium, and bivalent metals, 108.

DENTAL alloys, Analysis of, 296.
Distillation apparatus for osmium and ruthenium, 259.
Dry assaying for platinum metals, 249.
Dysprosia, 76.
Dysprosium.—*See* "Rare-earth metals."

ELECTROMAGNET, 6.
Erbia, 76.
Erbium.—*See* "Rare-earth metals."
Europium. — *See also* "Rare - earth metals."
—, Separation of, from other rare earths, 80.
—, Volumetric determination of, 82.

FERROMOLYBDENUM, Impurities in, 202.
—, Molybdenum in, 202.
Ferroniobium, Impurities in, 165.
—, Niobium and tantalum in, 165.
Ferrotantalum, Impurities in, 165.
—, Tantalum and niobium in, 165.
Ferrotitanium, Titanium in, 101.
Ferrotungsten, Impurities in, 216.
—, Tungsten in, 215.
Ferrovanadium, Impurities in, 143.
—, Vanadium in, 141.
Filter-pulp, Use of, 4.

GADOLINIUM.—*See* "Rare-earth metals."
Gallium, Compounds of, 60.
—, Detection of, in ores, 63.
—, Determination of, in aluminium, 65.
—, — —, — bauxite, 64.
—, — —, — germanite, 64.
—, Gravimetric determination of, 62.
—, Separation of, from aluminium (large amounts), 62.
—, — —, — —, chromium, indium, uranium, and rare earths, 61.
—, — —, — —, —, manganese, mercury, lead, bismuth, and thallium, 62.
—, — —, — cadmium, zinc, nickel, cobalt, manganese, thorium, beryllium, 61.
—, — —, — hydrogen-sulphide group, 61.
—, — —, — iron, 62.
—, — —, — silver, 61.
Gases, Determination of, in uranium ores, 236.
Germanium, Compounds of, 124.
—, Detection of, in ores, 127.
Germanium, Determination of, in germanite, 127.
—, — —, — zinc blende, 128.
—, Gravimetric determination of, 126.
—, Separation of, from arsenic and antimony, 126.
—, — —, — copper, bismuth, lead, and cadmium, 126.
—, — —, — other elements, 124.
Glucinum.—*See* "Beryllium."
Gold, Determination of, in the presence of platinum metals, 263.

HAFNIUM, 103.
—, Compounds, Detection, Determination, and Separation from other elements of.—*See* "Zirconium."
—, Separation of, from zirconium, 108.
— and zirconium, Indirect determination of, 109.
Helium in uranium ores, 236.
Holmia, 76.
Holmium.—*See* "Rare-earth metals."
Hydroxyquinoline (oxine) as a reagent for:
  Beryllium, Separation of, from aluminium, 48.
  Gallium, Gravimetric determination of, 63.
  Indium, Gravimetric determination of, 68.
  Molybdenum, Gravimetric determination of, 196.
  Rhenium, Separation of, from molybdenum, 239.

ILLINIUM, 75.
Ilmenite, Complete analysis of, 101.
Indium, Compounds of, 65.
—, Detection of, in ores, 68.
—, Determination of, in ores, 68.
—, Gravimetric determination of, 67.
—, Separation of, from arsenic, 66.
—, — —, — cadmium, zinc, copper, nickel, cobalt, and manganese, 67.
—, — —, — gallium, 67.
—, — —, — hydrogen-sulphide group, 66.
—, — —, — lead, 66.
—, — —, — manganese, aluminium, and iron, 67.
—, — —, — tin, antimony, and bismuth, 66.
Iridium.—*See also* "Platinum metals."
—, Complete analysis of, 294.
—, Compounds of, 242.
—, Gravimetric determination of, 280, 281.
—, Reactions of, 287.
—, Separation of, from lead, 265.
—, — —, — palladium, 278.
—, — —, — platinum, 277.
—, — —, — —, palladium, and rhodium, 272, 274.

Iridium, Separation of, from rhodium, 278.
—, — —, — ruthenium and osmium, 269.
— and platinum, Separation of, from palladium and rhodium, 275.

Jewellers' platinum alloys, 296.
Jones reductor, 4.

Lanthana, 76.
Lanthanum. — *See also* "Rare - earth metals."
—, Separation of, from praseodymium and neodymium, 80.
Lead button, Treatment of, for determination of platinum metals, 249.
Lepidolite, Analysis of, 41.
Lithium, Compounds of, 37.
—, Detection of, in minerals, 40.
—, Determination of, in minerals, 40.
—, Gravimetric determination of, 39.
—, Separation of, from alkaline earths, 38.
—, — —, — aluminium, 37.
—, — —, — magnesium, 38.
—, — —, — other alkali metals, 38, 43.
—, Volumetric determination of, 39.
Lutecia, 76.
Lutecium.—*See* "Rare-earth metals."
— lines, 109.

Magnetic minerals, 10.
— separation, 8.
Mineralogical analysis, 7, 9, 11, 12.
Molybdenite, Complete analysis of, 204.
Molybdenum, Colorimetric determination of, 199.
—, Compounds of, 190.
—, Detection of, in ores, 199.
—, — —, — steel, 200.
—, Determination of, in ferromolybdenum, 202.
—, — —, — molybdenite, 201, 202.
—, — —, — steel, 202.
—, — —, — wulfenite, 201.
—, Gravimetric determination of, 194.
—, Separation of, from antimony, 192.
—, — —, — arsenic, 192.
—, — —, — — and phosphorus, 192.
—, — —, — copper, 193.
—, — —, — iron, 191.
—, — —, — lead, 193.
—, — —, — phosphorus, arsenic, antimony, and vanadium, 193.
—, — —, — sulphur, 192.
—, — —, — tin, 193.
—, — —, — tungsten, 193.
—, — —, — vanadium, 193.
—, Volumetric determination of, 198.
— ores, Impurities in, 202.
Monazite, Complete analysis of, 85.

Neodymia, 76.
Neodymium.—*See also* "Rare - earth metals."
Neodymium, Separation of, from praseodymium, 81.
— and praseodymium, Separation of, from lanthanum, 80.
Nickel crucibles, Use of, 3.
Niobium, 145.
—, Compounds of, 146.
—, Detection of, in minerals, 161.
—, Determination of, in columbite, 163.
—, — —, — ferroniobium, 165.
—, — —, — tantalite, 163.
—, Gravimetric determination of, 158.
—, — micro-method for, 159.
—, Separation of, from aluminium, chromium, and manganese, 150.
—, — —, — ammonium-sulphide group metals, 149.
—, — —, — hydrogen-sulphide group metals, 148.
—, — —, — silica, 147.
—, — —, — tannin group B metals, 150.
—, — —, — tantalum, 154.
—, — —, — tin, 147.
—, — —, — titanium, 152.
—, — —, — tungsten, 151.
—, — —, — zirconium, 150.
—, Volumetric determination of, 160.
Nitrite process for platinum metals, 257.

Osmiridium, Complete analysis of, 293.
Osmium.—*See also* "Platinum metals."
—, Complete analysis of, 296.
—, Compounds of, 242.
—, Gravimetric determination of, 278.
—, Reactions of, 285.
—, Separation of, from all other elements, 269.
—, — —, — ruthenium, 276.
— and ruthenium, Separation of, from all other elements, 269.
Oxine.—*See* "Hydroxyquinoline."

Palladium. — *See also* "Platinum metals."
—, Colorimetric determination of, 283.
—, Complete analysis of, 294.
—, Compounds of, 242.
—, Gravimetric determination of, 281.
—, Reactions of, 288.
—, Separation of, from iridium, 278.
—, — —, — lead, 265.
—, — —, — platinum, 276.
—, — —, — —, iridium, and rhodium, 272.
—, — —, — rhodium, 278.
—, — —, — silver, 261.
Platinum, Colorimetric determination of, 282.
—, Complete analysis of native, 291.
—, — — — refined, 294.
—, — — — South African concentrates, 293.
—, Compounds of, 242.
—, Gravimetric determination of, 280.

Platinum, Reactions of, 288.
—, Separation of, from iridium, 277.
—, — —, — —, rhodium, and palladium, 273.
—, — —, — lead, 265.
—, — —, — palladium, 276.
—, — —, — rhodium, 276.
— and iridium, Separation of, from palladium and rhodium, 275.
— crucibles, Analysis of, 296.
— group, Detection of, in ores, 283.
— —, Qualitative analysis of, 15.
— —, Resolution of, into subgroups, 267.
— metals, Detection of, in ores, 283.
— —, Determination of, in base-metal ores, speisses, sweeps, and rocks, 288.
— —, — —, — copper - nickel ores, mattes, and copper bullion, 290.
— —, Separation of, from arsenic, antimony, selenium, and tellurium, 266.
— —, — —, — bismuth, 266.
— —, — —, — copper, 266.
— —, — —, — gold, 262.
— —, — —, — iron, nickel, zinc, etc., 267.
— —, — —, — silver, 261.
— —, — —, — —, gold, and base metals after lead fusion, 263.
Praseodymia, 76.
Praseodymium.—*See also* "Rare-earth metals."
—, Separation of, from neodymium, 81.
— and neodymium, Separation of, from lanthanum, 80.

QUALITATIVE analysis, General scheme of, 13.

RADIUM in uranium ores, 223.
Rare-earth group, Qualitative analysis of, 17.
— metal oxalates, 77.
— metals, Compounds of, 76.
— —, Detection of, in minerals, 83.
— —, Determination of, in minerals, 83.
— —, — —, — monazite, 85.
— —, Gravimetric determination of, 81.
— —, Separation of, from ammonia group metals and phosphoric acid, 77.
— —, — —, — earth acids, 85.
— —, — —, — one another, 78.
— —, — —, — scandium, 78.
— —, — —, — thorium, 78.
— —, Subdivision of, into groups, 75.
— —, Volumetric determination of, 81.
Rhenium, Compounds of, 238.
—, Detection of, in ores, 240.
—, Determination of, in ores, 240.
—, Gravimetric determination of, 239.
—, Separation of, by distillation, 239.
Rhenium, Separation of, from metals not precipitated by hydrogen sulphide, 238.
—, — —, — molybdenum, 239.
—, Volumetric determination of, 240.
Rhodium.—*See also* "Platinum metals."
—, Complete analysis of, 295.
—, Compounds of, 242.
—, Gravimetric determination of, 282.
—, Reactions of, 286.
—, Separation of, from iridium, 278.
—, — —, — lead, 265.
—, — —, — palladium, 278.
—, — —, — platinum, 276.
—, — —, — — and palladium, 275.
—, — —, — silver, 261.
Rubidium, Compounds of, 42.
—, Detection of, in minerals, 45.
—, Determination of, in minerals and rocks, 45.
—, Gravimetric determination of, 44.
—, Separation of, from other alkali metals, 43.
—, — —, — potassium, 42.
Ruthenium, Complete analysis of, 296.
—, Compounds of, 242.
—, Gravimetric determination of, 279.
—, Reactions of, 286.
—, Separation of, from osmium, 276.
— and osmium, Separation of, from all other elements, 269.
Rutile, Complete analysis of, 101.

SAMARIA, 76.
Samarium.—*See* "Rare-earth metals."
Scandium, Compounds of, 57.
—, Detection of, in minerals, 59.
—, Determination of, in minerals, 59.
—, — —, — thortveitite, 59.
—, — —, — wolframite, 59.
—, Gravimetric determination of, 59.
—, Separation of, from ceria earths, 58.
—, — —, — thoria, 58.
—, — —, — yttria earths, 58.
Scheelite, Complete analysis of, 219.
Selenide minerals, Complete analysis of rich, 188.
Selenium, 166.
—, Colorimetric determination of, 180.
—, Compounds of, 167.
—, Detection of, in ores, 182.
—, Determination of, in antimony and stibnite, 184.
—, — —, — chamber mud, 186.
—, — —, — commercial selenium, 187.
—, — —, — — tellurium, 187.
—, — —, — copper, 185.
—, — —, — electrolytic sludge, 185.
—, — —, — oxide ores, 185.
—, — —, — pyrites, 184.
—, — —, — rich anode slimes, 187.
—, — —, — sulphur, 186.
—, Gravimetric determination of, 177.
—, Interference of, in the determination of other metals, 170.

Selenium, Reactions of, of analytical importance, 170.
—, Separation of, from alkaline earths, copper, iron, etc., 174.
—, — —, — arsenic, antimony, tin, bismuth, etc., 172.
—, — —, — copper, 173.
—, — —, — gold, 173.
—, — —, — lead, 173.
—, — —, — mercury, 173.
—, — —, — nitric acid, 171.
—, — —, — non-volatile elements, 174.
—, — —, — silver, 172.
—, — —, — sulphur, 174.
—, — —, — tellurium, 176.
—, — process for, utilizing stannous chloride, 174.
—, Specific reactions of, 181.
—, Volumetric determination of, 179.
Silica crucibles, Use of, 3.
Silver, Determination of, in the presence of platinum metals, 262.
— bead, Nitric-acid parting of, 289.
— —, Sulphuric-acid parting of, 289.
— —, Treatment of, for platinum metals, 251–253.
Sodium hydroxide, Fusions with, 3.

TANNIN, Application of, in gravimetric analysis, 5.
— as a reagent for:
  Beryllium, Gravimetric determination of, 53.
  —, Separation of, from aluminium, 48.
  —, — —, — iron, 50.
  —, — —, — titanium, 51.
  —, — —, — zirconium, 52.
  Gallium, Gravimetric determination of, 62.
  —, Separation of, from bivalent metals, 61.
  Germanium, Gravimetric determination of, 126.
  —, Separation of, from bivalent metals, 125.
  Molybdenum, Detection of, 200.
  Niobium and tantalum, Detection of, 161.
  — — —, Determination of, in ores, etc., 164.
  — — —, Gravimetric determination of, 158.
  — — —, — micro-method for, 159.
  — — —, Identification of, 162.
  — — —, Separation of, from one another, 154.
  — — —, — —, — tannin group B metals, 150.
  — — —, — —, — titanium, 152.
  Tantalum.—*See* "Niobium and tantalum," *above*.
  Titanium, Determination of, in bauxite, 101.
  —, — —, — ilmenite, rutile, etc., 97.
  —, Gravimetric determination of, 94.
Tannin as a reagent for:
  Titanium, Separation of, from tannin groups B and C metals, 90.
  Tungsten, Determination of, in low-grade ores, 215.
  —, Gravimetric determination of, 212.
  Uranium, Colorimetric determination of, 230.
  —, Gravimetric determination of, 229.
  —, Separation of, from tannin group A metals, 225.
  Vanadium, Detection of, 139.
  —, Gravimetric determination of, 134.
  —, Separation of, from niobium, tantalum, and tungsten, 133.
  Zirconium, Gravimetric determination of, 111.
  —, Separation of, from tannin group A metals, 106.
  —, — —, — titanium, 107.
— groups A, B, and C, 6.
Tantalite, Complete analysis of, 166.
Tantalum, 145.
—, Compounds of, 146.
—, Detection of, in minerals, 161.
—, Determination of, in columbite, 163.
—, — —, — ferrotantalum, 165.
—, — —, — tantalite, 163.
—, Gravimetric determination of, 158.
—, — micro-method for, 159.
—, Separation of, from aluminium, chromium, and manganese, 150.
—, — —, — ammonium-sulphide group metals, 149.
—, — —, — hydrogen-sulphide group metals, 148.
—, — —, — niobium, 154.
—, — —, — silica, 147.
—, — —, — tannin group B metals, 150.
—, — —, — tin, 147.
—, — —, — titanium, 152.
—, — —, — tungsten, 151.
—, — —, — zirconium, 150.
—, Volumetric determination of, 160.
Telluride minerals, Complete analysis of rich, 188.
Tellurium, 166.
—, Compounds of, 167.
—, Detection of, in ores, 182.
—, Determination of, in commercial selenium, 187.
—, — —, — — tellurium, 187.
—, — —, — copper, 185.
—, — —, — electrolytic sludge, 185.
—, — —, — lead and galena, 185.
—, — —, — rich anode slimes, 187.
—, Gravimetric determination of, 178.
—, Interference of, in the determination of other metals, 170.
—, Reactions of, of analytical importance, 170.
—, Separation of, from alkaline earths, copper, iron, etc., 174.
—, — —, — arsenic, antimony, tin, bismuth, etc., 172.

Tellurium, Separation of, from copper, 173.
—, — —, — gold, 173.
—, — —, — lead, 173.
—, — —, — mercury, 173.
—, — —, — nitric acid, 171.
—, — —, — non-volatile elements, 174.
—, — —, — selenium, 176.
—, — —, — silver, 172.
—, — —, — sulphur, 174.
—, — process for, utilizing stannous chloride, 174.
—, Specific reactions of, 181.
—, Volumetric determination of, 180.
Terbia, 76.
Terbium.—*See also* "Rare-earth metals."
—, Approximate separation of, from terbia-group earths, 81.
— group, 75.
Thallium, 69.
—, Compounds of, 69.
—, Detection of, in ores, 73.
—, Determination of, in blende, 73.
—, — —, — minerals, 73.
—, — —, — pyrites, 73.
—, General separation procedure for, 71.
—, Gravimetric determination of, 72.
—, Separation of, from arsenic and antimony, 71.
—, — —, — gallium, indium, aluminium, iron, chromium, zinc, cadmium, nickel, cobalt, and selenium, 71.
—, — —, — lead, bismuth, and manganese, 71.
—, — —, — silver, mercury, and copper, 71.
—, — —, — tin, 71.
—, Volumetric determination of, 73.
Thorianite, Complete analysis of, 123.
Thorite, Complete analysis of, 123.
Thorium, Compounds of, 118.
—, Detection of, in ores, 121.
—, Determination of, in monazite, 121.
—, — —, — thorianite, 122.
—, — —, — thorite, 122.
—, Gravimetric determination of, 120.
—, Separation of, from other elements, 118.
—, — —, — the rare earths, 119.
Thulia, 76.
Thulium.—*See* "Rare-earth metals."
Titanium, Colorimetric determination of, 96.
—, Compounds of, 87.
—, Detection of, in minerals, 96.
—, Determination of, in bauxite, 101.
—, — —, — ferrotitanium, 101.
—, — —, — ilmenite, 97.
—, — —, — iron ores, 100.
—, — —, — rocks, 100.
—, — —, — rutile, 97.
—, Gravimetric determination of, 94.
Titanium, Separation of, from aluminium, chromium, uranium, manganese, nickel, cobalt, zinc, beryllium, and phosphoric acid, 92.
—, — —, — chromium, vanadium, molybdenum, and phosphorus, 93.
—, — —, — hydrogen-sulphide group metals, 89.
—, — —, — iron, zinc, nickel, cobalt, and manganese, 89.
—, — —, — niobium and tantalum, 152.
—, — —, — rare-earth metals, 77.
—, — —, — silica, 93.
—, — —, — tannin group B metals, 90.
—, — —, — thorium, 118.
—, — —, — tin, 89.
—, — —, — tungsten, 93.
—, — —, — zirconium, 106.
—, Volumetric determination of, 95.
Titanous salts as precipitants for platinum metals, 258.
Tungsten, Colorimetric determination of, 213.
—, Compounds of, 207.
—, Detection of, in ores, 213.
—, Determination of, in ferrotungsten, 215.
—, — —, — ores, 213, 216.
—, — — impurities in ferrotungsten and ores, 216.
—, Gravimetric determination of, 211.
—, Separation of, from aluminium, 210.
—, — —, — arsenic, 210.
—, — —, — iron, manganese, calcium, and heavy metals, 209.
—, — —, — molybdenum, 194, 218.
—, — —, — niobium and tantalum, 151.
—, — —, — phosphorus, 210.
—, — —, — silica, 209.
—, — —, — silver, 210.
—, — —, — tin, 210.
—, — —, — titanium, 93.
—, — —, — vanadium, 132, 133.
—, — —, — zirconium, thorium, rare earths, beryllium, and iron, 210.
—, Volumetric determination of, 212.
— ores, Complete analysis of, 220.
Tungstic oxide, Testing of, for purity, 211.

URANIUM, Colorimetric determination of, 230.
—, Compounds of, 222.
—, Detection of, in ores, 231.
—, Determination of, in carnotite, 232.
—, — —, — ores, 231.
—, Gravimetric determination of, 228.
—, Separation of, from aluminium, 226.
—, — —, — — and beryllium, 227.
—, — —, — —, chromium, manganese, and phosphoric acid, 224.

Uranium, Separation of, from beryllium, 52.
—, — —, — hydrogen-sulphide group metals, 223.
—, — —, — iron, nickel, cobalt, and zinc, 224.
—, — —, — —, titanium, cobalt, zinc, and manganese, 223, 224.
—, — —, — —, vanadium, titanium, and zirconium, 224.
—, — —, — nickel, beryllium, and alkaline earths, 224.
—, — —, — phosphoric and arsenic acids, 228.
—, — —, — titanium, niobium, and tantalum, 225.
—, — —, — vanadium, 227.
—, — —, — zirconium, 227.
—, — — uranic from uranous, 225.
—, Volumetric determination of, 230.
— ores, Complete analysis of, 235.
— —, Determination of gases in, 236.

VANADIUM, Colorimetric determination of, 138.
—, Compounds of, 130.
—, Detection of, in ores, 139.
—, Determination of, in carnotite, 233.
—, — —, — ferrovanadium, 141.
—, — —, — iron ores and rocks, 141.
—, — —, — ores, 139.
—, — —, — steel, 142.
—, Gravimetric determination of, 134.
—, Separation of, from aluminium, 134.
—, — —, — —, chromium, uranium, beryllium, manganese, zinc, and nickel, 131.
—, — —, — arsenic, molybdenum, and tungsten, 132.
—, — —, — chromium, 134.
—, — —, — hydrogen-sulphide group metals, 131.
—, — —, — iron, titanium, and zirconium, 131.
—, — —, — —, zinc, nickel, cobalt, and manganese, 131.
—, — —, — niobium, tantalum, and tungsten, 133.
—, — —, — phosphoric acid, 132.
—, — —, — silica, 134.
—, — —, — titanium, 131.
—, Volumetric determination of, 136.
— ores, Complete analysis of, 144.
— —, Determination of impurities in, 143.

WOLFRAMITE, Complete analysis of, 219.
Wulfenite, Complete analysis of, 205.

YTTERBIUM. — *See also* "Rare-earth metals."
—, Separation of, from other rare earths, 80.
Yttria, 76.
Yttrium.—*See* "Rare-earth metals."
— group, 75.
— —, Detection of, 83.
— —, Separation of, from cerium group, 78.

ZIRCON sand, Complete analysis of, 115.
Zirconium, 103.
—, Compounds of, 104.
—, Detection of, in minerals, 111.
—, Determination of, in Brazilian zirconia rock, 112.
—, — —, — rocks, 114.
—, — —, — zircon, 112.
—, Gravimetric determination of, 111.
—, Separation of, from aluminium, 108.
—, — —, — —, iron, rare earths, manganese, nickel, cobalt, zinc, copper, lead, and bismuth, 108.
—, — —, — —, uranium, chromium, beryllium, manganese, nickel, cobalt, and zinc, 108.
—, — —, — beryllium, 52.
—, — —, — hafnium, 108.
—, — —, — hydrogen-sulphide group metals, 105.
—, — —, — iron, zinc, nickel, cobalt, and manganese, 105.
—, — —, — niobium and tantalum, 106.
—, — —, — phosphorus, arsenic, vanadium, chromium, molybdenum, and tungsten, 108.
—, — —, — rare earths, 77.
—, — —, — silica, 108.
—, — —, — thorium, 118.
—, — —, — titanium, 107.
—, — —, — —, aluminium, iron, etc., 106.
—, — —, — —, niobium, and tantalum, 106.
— and hafnium, Indirect determination of, 109.

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